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Diffusion-reaction approach to electronic relaxation in solution. Exact solution for delta function sink models

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Abstract. We give a general method for finding the exact solution for the problem of electronic relaxation in solution, modelled by a particle undergoing diffusive motion in a potential in presence of a delta function sink. The diffusive motion is described by the Smoluchowski equation and the sink could be a delta function of arbitrary position and strength. The solution requires the knowledge of the Laplace transform of the Green's function for the motion in the absence of the sink. We use the method to find the solution of the problem in the case where the diffusive motion is on a parabolic potential. This has been an unsolved problem for some time and is of considerable importance as a model for non-radiative electronic relaxation of a molecule in solution. The solution is analyzed to obtain the viscosity and temperature dependences of the rate constants.

Keywords. Electronic relaxation in solution; delta function sink model; Smoluchowski equation.

1. Introduction

Relaxation of an excited electronic state of a molecule which is in a polar solvent is of great current interest, both from experimental and theoretical points of view. See Lippert *et al* (1987) and Bagchi and Fleming (1990) for recent surveys. A molecule immersed in a liquid is put on an excited state potential energy surface (PES) by the absorption of radiation. The molecule executes a walk on the PES which may be taken to be random, as it is immersed in the solvent. As it moves, it may undergo non-radiative decay from certain regions of the surface. It may also undergo radiative decay from anywhere on the surface. From the theoretical point of view, the problem is to calculate the probability that the molecule will still be in the excited state, after a time t.

We denote the probability that the molecule would survive on the excited PES by $P_e(t)$. 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 de-excitation of the molecule as the absorption of the particle. It is also usual to assume that the motion on the PES is overdamped. Thus, the probability $P(x,t)$, that the particle may be found at x at the time t obeys a modified Smoluchowski equation (Bagchi *et al* 1983; Sumi and Marcus 1986; Bagchi 1987)

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

In the above,

$$\mathscr{L} = A\frac{\partial^2}{\partial x^2} + \frac{A}{k_B T}\frac{\partial}{\partial x}\frac{\mathrm{d}V(x)}{\mathrm{d}x}. \tag{2}$$

$V(x)$ is a potential causing the drift of the particle, and is determined by the shape of the excited PES. $S(x)$ is a position-dependent sink function, taken to be normalized (i.e. $\int_{-\infty}^{\infty} S(x)\mathrm{d}x = 1$), for convenience. 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. It is related to the friction coefficient ζ by $A = k_B T/\zeta$. Further, one can take ζ to be proportional to the viscosity η of the medium. The molecule is initially on the ground state PES, and as the liquid is at a temperature T, its distribution over the coordinate x is random. From this it undergoes Franck–Condon excitation to the upper state PES. Therefore, x_0, the initial position of the particle, on the excited state PES is random. We take it to be given by $P_0(x_0)$.

Even if one can determine $P_e(t)$, one still has the problem of defining a rate constant for the decay process. As is the usual case, the decay is almost never exponential over the entire time scale. Therefore, one can define rate constants in different ways. Bagchi *et al* (1983) make use of a long time rate constant $k_L = -\lim_{t\to\infty}(\mathrm{d}/\mathrm{d}t)\ln P_e(t)$ and an average rate constant k_I by $k_I^{-1} = \int_0^{\infty}\mathrm{d}t P_e(t)$. For an alternate definition of rate constants, see Sumi and Marcus (1986).

A few model problems for which exact solutions have been found are available in the literature. They are:

(1) *The instantaneous death models* (see Bagchi 1987a). In the Oster–Nishijima (1956) model, one assumes that the particle moves freely in the region where $0 < x < a$, while if it goes out of this region, it deeays with unit probability. On the other hand, in the staircase model, the particle is reflected at $x = 0$, but absorbed at $x = a$. Notice that in both cases the potential is flat if $0 < x < a$, i.e. $V(x) = 0$.

(2) *The pinhole sink model.* Here one has a hole of width tending to zero on the PES. See references Bagchi (1987a) and Schulten *et al* (1980). On reaching this, the particle would fall into it with probability one. Mathematically, it is taken to be a delta function of infinite strength. Solution can be obtained, even in the case where $V(x)$ is parabolic, provided the sink is at the origin. That is, $V(x) = Bx^2/2$, $S(x) = \delta(x)$ and $k_0 \to \infty$. In this limit, the effect of the sink is to make $P(0, t) = 0$ at all time. Thus one simply solves

$$\frac{\partial P(x,t)}{\partial t} = \mathscr{L}P(x,t) - k_r P(x,t), \tag{3}$$

subject to $P(0, t) = 0$! This equation can be solved quite easily by the method of images and from the solution one can obtain $P_e(t)$, k_I and k_L. Cases where the sink is not at the origin and is not of infinite strength are interesting and have been studied (Bagchi 1987). However, the investigation has been numerical and was found to converge slowly in the limit of large k_0. In the following, we give a general procedure for finding the exact solution of the problem with a delta function sink, and apply it to the case of a parabolic potential. A preliminary report of this work has already been made (Sebastian 1992). Solutions have been obtained for other, related problems by the same method (Chakravarti and Sebastian 1993). As it is possible to find exact expressions for the rate constants for motion on a realistic (parabolic) surface, the model should be of interest to any one interested in reaction dynamics.

2. Exact results for the delta function sink

We find it convenient to define the Laplace transform $\mathscr{P}(x,s)$ of $P(x,t)$ by

$$\mathscr{P}(x,s)=\int_0^\infty P(x,t)e^{-st}\mathrm{d}t. \tag{4}$$

Laplace transformation of (1) gives

$$[s-\mathscr{L}+k_0S(x)+k_r]\mathscr{P}(x,s)=P_0(x). \tag{5}$$

As k_r is a constant, the solution of this equation may be expressed in terms of the Green's function $\mathscr{G}(x,s|x_0)$, which obeys the equation

$$[s-\mathscr{L}+k_0S(x)]\mathscr{G}(x,s|x_0)=\delta(x-x_0). \tag{6}$$

$\mathscr{G}(x,s|x_0)$ describes motion in the case where there is no radiative decay. In terms of this, solution of (5) is

$$\mathscr{P}(x,s)=\int_{-\infty}^{\infty}\mathrm{d}x_0\mathscr{G}(x,s+k_r|x_0)P_0(x_0). \tag{7}$$

Using the operator notations of quantum mechanics, we can write

$$\mathscr{G}(x,s|x_0)=\langle x|[s-\mathscr{L}+k_0S]^{-1}|x_0\rangle, \tag{8}$$

where $|x\rangle(|x_0\rangle)$ denotes the position eigenket with an eigenvalue k (x_0). Now we use the operator identity

$$[s-\mathscr{L}+k_0S]^{-1}=[s-\mathscr{L}]^{-1}-[s-\mathscr{L}]^{-1}k_0S[s-\mathscr{L}+k_0S]^{-1}, \tag{9}$$

to obtain

$$\mathscr{G}(x,s|x_0)=\langle x|[x-\mathscr{L}]^{-1}|x_0\rangle-\langle x|[s-\mathscr{L}]^{-1}k_0S[s-\mathscr{L}+k_0S]^{-1}|x_0\rangle. \tag{10}$$

Inserting the resolution of identity $I=\int_{-\infty}^{\infty}\mathrm{d}y|y\rangle\langle y|$ in between the two inverses in the second term of the above equation, we arrive at a Lippman–Schwinger type equation

$$\mathscr{G}(x,s|x_0)=\mathscr{G}_0(x,s|x_0)-k_0\int_{-\infty}^{\infty}\mathrm{d}y\mathscr{G}_0(x,s|y)S(y)\mathscr{G}(y,s|x_0). \tag{11}$$

$\mathscr{G}_0(x,s|x_0)$ is defined by

$$\mathscr{G}_0(x,s|x_0)=\langle x|[s-\mathscr{L}]^{-1}|x_0\rangle \tag{12}$$

and 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 the time t, given that there is no decay. It obeys the diffusion equation

$$[(\partial/\partial t)-\mathscr{L}]G_0(x,t|x_0)=\delta(x-x_0). \tag{13}$$

The above equation has no sink term in it. As there is no sink, there is no absorption of the particle. Therefore, $\int_{-\infty}^{\infty}\mathrm{d}x\,G_0(x,t|x_0)=1$. From this one concludes that

$$\int_{-\infty}^{\infty}\mathrm{d}x\,\mathscr{G}_0(x,s|x_0)=1/s, \tag{14}$$

a result that we make use of in the following. If $S(y)=\delta(y-x_s)$, then (11) becomes

$$\mathscr{G}(x,s|x_0)=\mathscr{G}_0(x,s|x_0)-k_0\mathscr{G}_0(x,s|x_s)\mathscr{G}(x_s,s|x_0). \tag{15}$$

We now solve (15) to find

$$\mathscr{G}(x_s,s|x_0)=\mathscr{G}_0(x_s,s|x_0)[1+k_0\mathscr{G}_0(x_s,s|x_s)]^{-1}. \tag{16}$$

This, when substituted back into (15) gives

$$\mathscr{G}(x,s|x_0)=\mathscr{G}_0(x,s|x_0)-k_0\mathscr{G}_0(x,s|x_s)\mathscr{G}_0(x_s,s|x_0)[1+k_0\mathscr{G}_0(x_s,s|x_s)]^{-1}. \tag{17}$$

Using the above equation in (7) gives us $\mathscr{P}(x,s)$ explicitly, which we do not write down, as our interest is only in the survival probability $P_e(t)=\int_{-\infty}^{\infty}\mathrm{d}x P(x,t)$. It is possible to calculate the Laplace transform $\mathscr{P}_e(s)$ of $P_e(t)$, directly. $\mathscr{P}_e(s)$ is related to $\mathscr{P}(x,s)$ by $\mathscr{P}_e(s)=\int_{-\infty}^{\infty}\mathrm{d}x\mathscr{P}(x,s)$. Therefore, from (7), (14) and (17), we get

$$\mathscr{P}_e(s)=\frac{1}{s+k_r}\left[1-[1+k_0\mathscr{G}_0(x_s,s+k_r|x_s)]^{-1}k_0\times\int_{-\infty}^{\infty}\mathrm{d}x_0\mathscr{G}_0(x_s,s+k_r|x_0)P_0(x_0)\right]. \tag{18}$$

The average and long time rate constants may be found from $\mathscr{P}_e(s)$. Thus, $k_I^{-1}=\mathscr{P}_e(0)$ and $k_L=$ negative of the pole of $\mathscr{P}_e(s)$, closest to the origin. From (18), we get

$$k_I^{-1}=\frac{1}{k_r}\left[1-k_0[1+k_0\mathscr{G}_0(x_s,k_r|x_s)]^{-1}\int_{-\infty}^{\infty}\mathrm{d}x_0\mathscr{G}_0(x_s,k_r|x_0)P_0(x_0)\right]. \tag{19}$$

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

The expressions that we have obtained for $\mathscr{P}_e(s)$, k_I and k_L are quite general and are valid for any $V(x)$. However, their utility is limited by the fact that in order to make use of them one must know $\mathscr{G}_0(x,s|x_0)$, which is somewhat difficult to determine. It is possible to find $\mathscr{G}_0(x,s|x_0)$ only in a few limited cases and the parabolic potential is one of them.

3. The parabolic potential

3.1 *Green's function $\mathscr{G}_0(x,s|x_0)$*

In the following, we given results for the parabolic potential, where we take $V(x) = \mu\omega^2 x^2/2$, μ being the mass and ω the frequency. In this case, the equation obeyed by $\mathscr{G}_0(x,s|x_0)$ is

$$\left[s - A\frac{\partial^2}{\partial x^2} - \frac{\partial}{\partial x}Bx\right]\mathscr{G}_0(x,s|x_0) = \delta(x - x_0), \tag{20}$$

with $B = \mu\omega^2 A/(k_B T) = \mu\omega^2/\zeta$. We now introduce the variable z by $z = x(A/B)^{1/2}$, when we obtain

$$\left[v + \frac{d^2}{dz^2} + \frac{d_z}{dz}\right]\mathscr{G}_0(z,s|z_0) = -\delta(z - z_0)/(AB)^{1/2}, \tag{21}$$

where we have expressed the Green's function in terms of the new variable z. We have also introduced $z_0 = x_0(A/B)^{1/2}$ and $v = -s/B$. The homogeneous equation corresponding to (21) is well known in mathematical physics and has solutions in terms of the parabolic cylinder functions. The Green's function can therefore be expressed in terms of the parabolic cylinder functions as

$$\mathscr{G}_0(x,s|x_0) = F(z,s|z_0)/s, \tag{22}$$

with

$$F(z,s|z_0) = D_v(-z_<)D_v(z_>)\exp[(z_0^2 - z^2)/4]\Gamma(1-v)[B/(2\pi A)]^{1/2}. \tag{23}$$

See the appendices A and B for details.

3.2 *Rate constants*

To get a qualitative ideal of the behaviour 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

$$k_I^{-1} = k_r^{-1}[1 - k_0 F(z_s, k_r|z_0)/[k_r + k_0 F(z_s, k_r|z_s)]]. \tag{24}$$

Further,

$$k_L = -[\text{value of } s \text{ for which } s + k_0 F(z_s, s|z_s) = 0] + k_r. \tag{25}$$

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 (24) and (25) simplify. This is the limit studied by Bagchi and coworkers (Bagchi *et al* 1983; Bagchi 1987a). By analyzing this limit we arrive at conclusions which we expect to be valid for finite, but small k_r. We now consider the limit $k_r \to 0$ in (24). As one has $D_v(z) = \exp(-z^2/4)$ in the limit $v \to 0$, 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 $k_0 F(z_s, k_r|z_0)/[k_r + k_0 F(z_s, k_r|z_s)] \to 1$. Hence from (25), one gets

$$k_I^{-1} = \lim_{k_r \to 0} \frac{1}{k_r}\Big[(k_0 F(z_s, k_r|z_0)/[k_r + k_0 F(z_s, k_r|z_s)])_{k_r = 0}$$

$$- k_0 F(z_s, k_r|z_0)/[k_r + k_0 F(z_s, k_r|z_s)]\Bigg]$$

$$= -\left[\frac{\partial}{\partial k}(k_0 F(z_s, k_r|z_0)/[k_r + k_0 F(z_s, k_r|z_s)])\right]_{k_r=0} \tag{26}$$

$$= \Bigg[F(z_s, k_r|z_0)/[k_0[F(z_s, k_r|z_s)]^2]$$

$$- \frac{\partial}{\partial k_r}(F(z_s, k_r|z_0)/F(z_s, k_r|z_s))\Bigg]_{k_r=0} \tag{27}$$

$$= \exp(z_s^2/2)/\{k_0[B/(2\pi A)]^{1/2}\}$$

$$- \left[\frac{\partial}{\partial s}(\mathscr{G}(z_s, s|z_0)/\mathscr{G}(z_s, s|z_s))\right]_{s=0}. \tag{28}$$

We take, without loss of generality, $z_0 < z_s$, so that the particle is initially placed to the left of the sink. After somewhat lengthy algebra, we get

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

$$+ \left[\int_{z_0}^{z_s} \mathrm{d}z \exp(z^2/2)\mathrm{d}z(1 + \mathrm{erf}(z/\sqrt{2}))\right](\pi/2)^{1/2}/B, \tag{29}$$

in the limit $k_0 \to \infty$, the particle would be absorbed with certainty if it reaches x_s. This is referred to as the pinhole sink. In this limit, the first term on the right hand side vanishes and the expression reduces to that of Poornimadevi and Bagchi (1988), obtained by calculating the mean first passage time. Note that the first term in the above equation is a correction to their equation, for finite k_0. Even for diffusive motion in a general potential, this type of result is valid as is proved in appendix C.

As in Bagchi and Fleming (1990), viscosity and temperature dependence of the rate constants, k_I and k_L may be obtained by making the identification $A = kT/\zeta$ and $B = \mu\omega^2/\zeta$, with ζ being proportional to the viscosity η. Note that A/B is independent of the viscosity. It is convenient to introduce the dimensionless rate constants $\bar{k}_I$ and $\bar{k}_L$ by $\bar{k}_I = k_I/B$ and $\bar{k}_L = k_L/B$ and the dimensionless rate for non-radiative decay, $\bar{k}_0 = k_0/(AB)^{1/2}$. We depart slightly from the definition of the earlier paper (Sebastian 1992) in that this does not have $(2\pi)^{1/2}$ in it. In terms of them, (29) becomes

$$\bar{k}_I^{-1} = \exp(z_s^2/2)/[\bar{k}_0 + (2\pi)^{1/2}]\left[\int_{z_0}^{z_s} \mathrm{d}z \exp(z^2/2)\mathrm{d}z(1 + \mathrm{erf}(z/\sqrt{2}))\right](\pi/2)^{1/2}. \tag{30}$$

In the low viscosity or small $\bar{k}_0$ limit, $\bar{k}_0 \ll 1$, only the first term on the RHS of (30) is significant. k_I is then independent of η. If the sink is not at the origin, $z_s \neq 0$, and the rate exhibits Arrhenius type activation. But if $z_s \approx 0$, k_I would decrease with temperature, leading to an apparently 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 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 satisfies $s + k_0 F(z_s, s|z_s) = 0$. Explicitly, $k_L = -s$. Using (23) we written this equation as an equation for v $(= -s/B)$,

$$v/\bar{k}_0 = D_v(-z_s)D_v(z_s)D_v(z_s)\Gamma(1-v)/(2\pi)^{1/2}. \tag{31}$$

If $v = n$, where $n = 0, 1, 2, \ldots, D_v(z) = 2^{-(n'2)}\exp(-z^2/4)H_n(z/\sqrt{2})$, H_n being Hermite polynomials. $\Gamma(1-v)$ has simple poles at $v = 1, 2, \ldots$. A graphical analysis of (31) using the above data is shown in figure 1, where we plot both the sides of the equation as functions of v. This leads to the conclusion that there is one value of $v \in [n, n+1]$ which satisfies (31). As we are analyzing the long time limit, our interest is only in $v \in [0, 11]$. If $\bar{k}_0 \ll 1$ then this value of $v \ll 1$ and one may approximate it by zero on the right hand side of (31) to get $v \approx \bar{k}_0 D_0(-z_s)D_0(z_s)/(2\pi)^{1/2}$ and hence

$$k_L = \exp(-z_s^2/2)k_0[B/(2\pi A)]^{1/2}. \tag{32}$$

In this case decay is only a small perturbation and is, consequently, from the equilibrium population. In this limit, the rate constant, k_L exhibits Arrheniu activation and is independent of η. If $\bar{k}_0 \gg 1$, the left hand side of (31) is small and the value of v is now given by $D_v(-z_s)D_v(z_s)\Gamma(1-v) \approx 0$ so that v is determined by $D_v(-z_s)D_v(z_s) = 0$. If $|v| < 1$, $D_v(z_s) = 0$ only for $z < 0$ (Erdélyi 1953), and hence we write this as $D_v(-|z_s|) = 0$. If $\bar{k}_0 = \infty$ and $z_s = 0$, one gets $v = 1$ and hence $k_L = B$, the result for the pinhole sink at the origin (Bagchi and Fleming 1990; Bagchi 1987a). However, for any other value of $\bar{k}_0$ and z_s, one has a solution of (31) with $v < 1$. If $z_s \gg 1$ (we take it to be positive without loss of generality), then again one can obtain an analytic solution to (31). For this, we substitute the asymptotic expressions $D_v(z_s) = \exp(-z_s^2/4)z_s^v[1 + O(1/z_s^2)]$ and $D_v(-z_s) = \exp(-z_s^2/4)z_s^v[1 + O(1/z_s^2)] + \exp(-z_s^2/4)z_s^{-v-1}/(2\pi)^{1/2}[1 + O(1/z_s^2)]/\Gamma(-v)$ into (31), use $-v\Gamma(-v) = \Gamma(1-v)$,

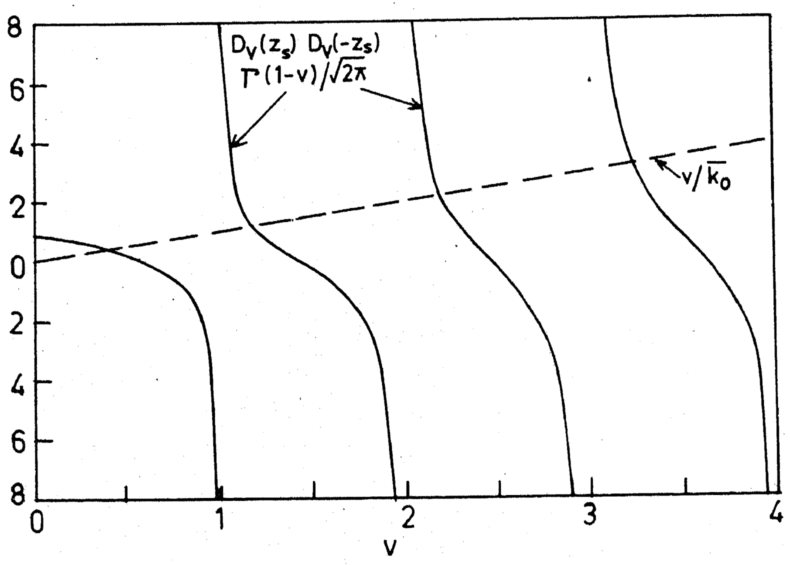

Figure 1. Plots of $v/\bar{k}_0$ (-----) and $D_v(-z_s)D_v(z_s)\Gamma(1-v)/(2\pi)^{1/2}$ (——) against v for $\bar{k}_0 = 1$ and $z_s = 0{\cdot}5$.

and solve for v, to obtain

$$\frac{v}{\bar{k}_0} = \frac{z_s \exp(-z_s^2/2)}{(\bar{k}_0 + z_s)\sqrt{2\pi}} [1 + O(1/z_s^2)]. \tag{33}$$

If one has decay from an equilibrium situation, with $z_s \gg \bar{k}_0$, then $z_s/(\bar{k}_0 + z_s) \approx 1$ and the above equation gives (32). On the other hand, if $z_s \ll \bar{k}_0$, then $z_s/(\bar{k}_0 + z_s) \ll 1$ and the long time rate is much lower than the equilibrium rate. This happens because the particle is absorbed as soon as it reaches the sink so that the population in the vicinity of the sink deviates strongly from the equilibrium one. However, it still has an Arrhenius dependence!

From the above analysis, one finds the following viscosity dependence for the rate constants (see Bagchi and Fleming 1990 and Bagchi 1987b).

Viscosity dependence of the rate constants

	k_L	k_I
$\bar{k}_0 \ll 1$	Independent	Independent
$z_s \gg \bar{k}_0 \gg 1$	Fractional	Fractional
$\bar{k}_s \gg z_s$	Inverse	Inverse

3.3 *Numerical results*

In the following we give numerical results for the problem, with the aim of illustrating the major results. On the whole, these confirm the numerical results of Bagchi (1987a). In the $k_r \to 0$ limit, there are only three dimensionless parameters for the problem. They are $\bar{k}_0$, z_s and z_0. Therefore, we study the long term and average rate constants as a function of these parameters. In figure 2, we plot $(\bar{k}_L/\bar{k}_0)$ against $\exp(-z_s^2/2)(2\pi)^{1/2}$ for two values of $\bar{k}_0$, viz 0·1 and 10·0. For $\bar{k} = 0{\cdot}1$, the result is a straight line with a slope of unity, as predicted by (32). On the other hand, for $\bar{k}_0 = 10$, one has a limit where deviation from the equilibrium population is important. The dotted line in the figure is a plot of $z_s \exp(z_s^2/2)/[(k_0 + z_s)(2\pi)^{1/2}]$ and there is good agreement between this approximate result and the actual one (dashed line) for large z_s. On a $\log(\bar{k}_L/\bar{k}_0)$ vs $-z_s^2/2$ plot the two curves are almost coincident. Figure 3 shows the plot of $\log(\bar{k}_I)$ against $\log(\bar{k}_0)$, for two values of z_0, z_s being kept constant. The plot demonstrates the dependence of $\bar{k}_I$ on z_0, explicitly. Plotted in the same figure are the values of $\log(\bar{k}_L)$, for the same value of z_s. For small $\bar{k}_0$, $\bar{k}_L \approx \bar{k}_I$, while for large $\bar{k}_0$, the two could be different. In fact they are closer to one another, if the position of the sink is not near the initial position of the particle, so that the particle decay takes a longer time.

4. Summary and conclusions

We have given a general procedure for solving the problem of radiationless decay, modelled by a modified Smoluchowski equation, with a delta function sink. The

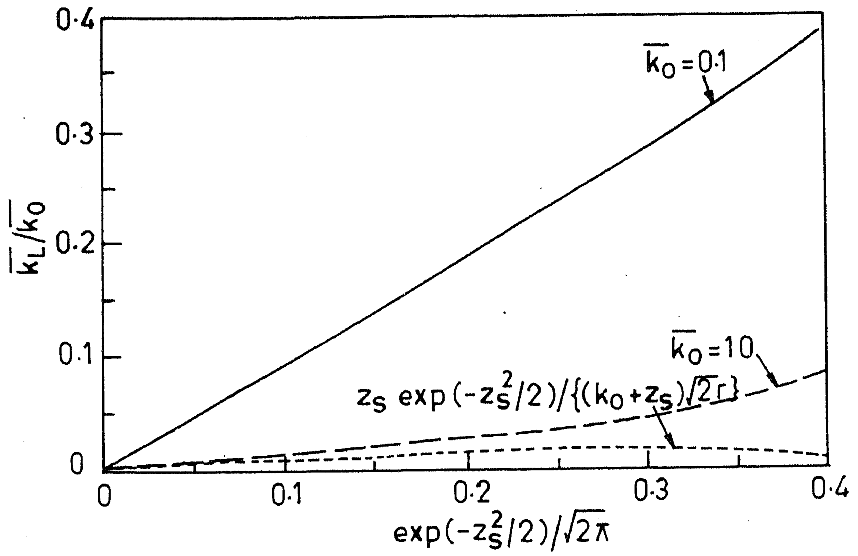

Figure 2. Plot of $\bar{k}_L/\bar{k}_0$ vs $\exp(-z_s^2/2)/(2\pi)^{1/2}$ for $\bar{k}_0 = 0{\cdot}1$ (——) and $\bar{k}_0 = 10$ (---). The line (------) is the plot of $z_s \exp(-z_s^2/2)/[(\bar{k}_0 + z_s)(2\pi)^{1/2}]$.

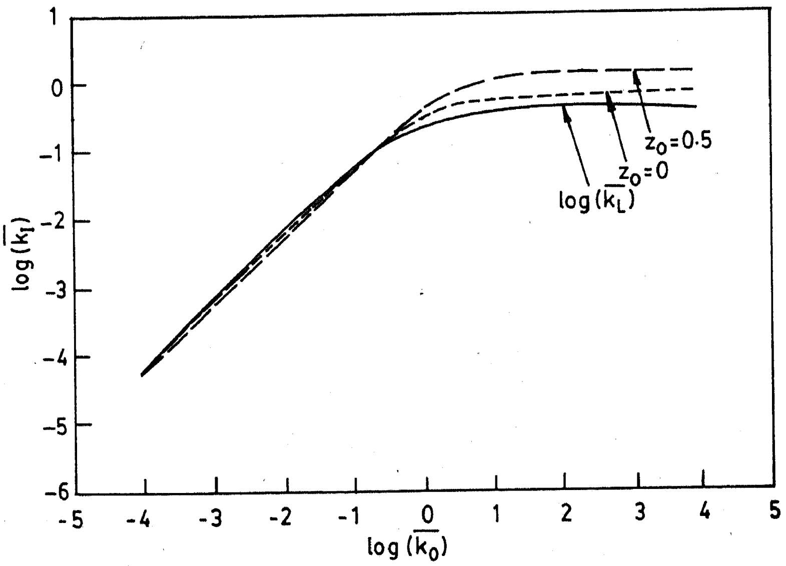

Figure 3. Log($\bar{k}_I$) against log($\bar{k}_0$) for $z_0 = 0{\cdot}5$ (---), $z_0 = 0$ (------), for $z_s = 1$. (——) is the plot of log($\bar{k}_L$).

procedure is applicable to any problem for which Green's function for the motion in the absence of the sink is known. Expressions for k_I and k_L applicable in the general case have been given. The method has been applied to the problem where motion takes place on a parabolic potential, for which the Green's function can be found. Explicit expressions for k_I and k_L for arbitrary values of k_r have been given. The $k_r \to 0$ limit has been analyzed in detail. In this limit, the problem has three dimensionless parameters, which are related to the sink position, initial position of the particle and the rate of non-radiative decay. Analytical and numerical results have been presented for various values of these parameters.

Our equation (11) is quite general and we have used it to solve other related problems, involving delta function sinks, for which $\mathscr{G}_0(x,s|x_0)$ is known (Chakravarti and Sebastian 1993). The same procedure is also applicable to the case where S is a non-local operator, and may be represented by $S \equiv |f\rangle k_0 \langle g|$, f and g are arbitrary acceptable functions. Choosing both of them to be Gaussian should be an improvement over the delta function sink model. S may even be a linear combination of such operators.

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Appendix A. Determination of $\mathscr{G}_0(x,s|x_0)$

We follow Courant and Hilbert (1953). Equation (21) is

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}z^2}+\frac{\mathrm{d}}{\mathrm{d}z}z+\nu\right]\mathscr{G}_0(z,s|z_0) = -\delta(z-z_0)/(AB)^{1/2}. \tag{A1}$$

We solve this equation separately for $z > z_0$ and $z < z_0$ and match them properly at $z = z_0$.

Region 1: $z > z_0$. In this region, the equation reads

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}z^2}+\frac{\mathrm{d}}{\mathrm{d}z}z+\nu\right]\mathscr{G}_0(z,s|z_0) = 0. \tag{A2}$$

We need a solution, that will approach zero as $z \to \infty$. The two independent solutions of the equation are $\exp(-z^2/4)D_\nu(z)$ and $\exp(-z^2/4)D_\nu(-z)$ (see appendix B). Of these, the second one is unacceptable as it tends ∞ as z tends to ∞. Therefore we take the solution to be $\mathscr{G}_0(z,s|z_0) = (\text{constant})\exp(-z^2/4)D_\nu(z)$. We write the constant as $C_1/[\exp(-z_0^2/4)D_\nu(z_0)]$ so that

$$\mathscr{G}_0(z,s|z_0) = C_1\exp(-z^2/4)D_\nu(z)/[\exp(-z_0^2/4)D_\nu(z_0)], \tag{A3}$$

C_1 is yet to be determined.

Region 2: $z < z_0$. In this region again, (A1) reduces to (A2) above. Here, we need the solution, that will approach zero as z tends to $-\infty$. We take the solution to be

$$\mathscr{G}_0(z,s|z_0) = C_2\exp(-z^2/4)D_\nu(-z)/[\exp(-z_0^2/4)D_\nu(-z_0)], \tag{A4}$$

C_2 is to be determined. The differential equation (1) implies that $\mathscr{G}_0(z,s|z_0)$ is continuous at z_0, which gives $C_1 = C_2$. Further, it also implies

$$\left[\frac{\mathrm{d}}{\mathrm{d}z}\exp(z^2/2)\mathscr{G}_0(z,s|z_0)\right]_{z_0-\varepsilon}^{z_0+\varepsilon} = -\exp(z_0^2/2)/(AB)^{1/2}, \tag{A5}$$

for infinitesimal positive ε. Using (A3) and (A4) to evaluate the LHS of (5), and using (B2) we get

$$C_1 = \Gamma(-\nu)D_\nu(z_0)D_\nu(-z_0)/(2\pi AB)^{1/2}. \tag{A6}$$

Γ is the Gamma function. Using the identity $\Gamma(-\nu) = \Gamma(1-\nu)/(-\nu)$, we write

$$\mathscr{G}_0(x, s|x_0) = F(z, s|z_0)/s, \tag{A7}$$

with

$$F(z, s|z_0) = D_\nu(-z_<)D_\nu(z_>)\exp[(z_0^2 - z^2)/4]\Gamma(1-\nu)[B/(2\pi A)]^{1/2}, \tag{A8}$$

$z_< = \min(z, z_0)$ and $z_> = \max(z, z_0)$.

Appendix B. Properties of the parabolic cylinder function used in the paper

Here we give only those properties that are relevant to us. Details may be found in Erdélyi (1953), Whittaker and Watson (1962). $D_\nu(z)$ and $D_\nu(-z)$ both obey the differential equation

$$\frac{d^2D}{dz^2} + \{\nu + 1/2 - z^2/4\}D_\nu = 0. \tag{B1}$$

Their Wronskian is

$$D_\nu(z)\frac{dD(-z)}{dz} - D_\nu(-z)\frac{dD(z)}{dz} = (2\pi)^{1/2}/\Gamma(-\nu). \tag{B2}$$

In Magnus *et al* (1966), a factor of $\sqrt{2}$ is missing in this equation. If $\mathrm{Re}(\nu) < 0$, then $D_\nu(z)$ has the integral representation

$$D_\nu(z) = [\exp(-z^2/4)/\Gamma(-\nu)] \int_0^\infty dt \exp[-(t^2/2 + zt)]t^{-\nu-1}. \tag{B3}$$

For $\mathrm{Re}(\nu) > 0$, other integral representations are available. Alternatively, it may be defined by the recursion

$$D_{\nu+1}(z) = zD_\nu(z) - \nu D_{\nu-1}(z). \tag{B4}$$

For real $z > 0$, $D_\nu(z) = \exp(-z^2/4)z^\nu[1 + \mathcal{O}(1+z^2)$ and] $D_\nu(-z) = \exp(-z^2/4)z^2[1 + O(1/z_s^2) + \exp(-z^2/4)z^{-\nu-1}(2\pi)^{1/2}[1 + O(1/z^2)]]/\Gamma(-\nu)$. For $\nu = 0$, one has

$$D_0(z) = \exp(-z^2/4). \tag{B5}$$

Appendix C

In this appendix, we give an interesting result for k_I mentioned in the paper. An equation similar to (29) is valid for dynamics on an arbitrary potential $V(x)$, in presence of a delta function sink. The proof is given below. Our equation (27) holds for an arbitrary $V(x)$, provided we take $F(z, s|z_0)$ to be defined by (22). We now make use of the following: $\lim_{s\to 0} F(z, s|z_0) = \lim_{s\to 0} s\mathscr{G}(z, s|z_0) = \lim_{t\to\infty} G(z, t|z_0) =$ the equilibrium probability distribution, $P_e(z)$, which obeys $\mathscr{L}P_e(z)=0$. On solving this, we get $P_e(z)=\exp[-V(x)/(k_B T)]N$, where

$$N^{-1}=\int_{-\infty}^{\infty}\exp[-V(x)/(k_B T)]\mathrm{d}x. \tag{C1}$$

Using this in (27)

$$k_I^{-1}=\exp[V(x)/(k_B T)]/(k_0 N)-\left[\frac{\partial}{\partial s}\mathscr{G}(z_s,k_r|z_0)/\mathscr{G}(z_s,k_r|z_s)\right]_{s=0}. \tag{C2}$$

$\mathscr{G}(x,k_r|x_0)$ obeys the equation

$$\left\{s-A\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\frac{A}{k_B T}\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{\partial V(x)}{\partial x}\right]\right\}\mathscr{G}(x,s|x_0)=\delta(x-x_0). \tag{C3}$$

We make the substitution $\mathscr{G}_0(x,s|x_0)=\exp[-V(x)/(2k_B T)]\mathscr{X}(x,s|x_0)$ to obtain

$$\left\{s-A\frac{\mathrm{d}^2}{\mathrm{d}x^2}-U(x)\right\}\mathscr{X}(x,s|x_0)=\exp[-V(x_0)/(2k_B T)]\delta(x-x_0). \tag{C4}$$

In the above, we have defined $U(x)=A[2d^2V/\mathrm{d}x^2-(\mathrm{d}V/\mathrm{d}x)^2/k_B T]/(4k_B T)$. Now following the standard procedure of Courant and Hilbert (1953), we introduce $y_i(x,s)$, $i=1,2$ obeying

$$\left\{s-A\frac{\mathrm{d}^2}{\mathrm{d}x^2}-U(x)\right\}y_i(x,s|x_0)=0, \tag{C5}$$

and satisfying the conditions $y_1(-\infty)=0$ and $y_2(\infty)=0$ Then one can write

$$\mathscr{X}(x,s|x_0)=C_1 y_1(x_<)y_2(x_>,s), \tag{C6}$$

where $x_<=\min(x,x_0)$ and $x_>=\max(x,x_0)$. C_1 is determined to be $C_1=\exp[V(x_0)/(2k_B T)]/[AW\{y_1,y_2\}]$, where $W\{y_1,y_2\}$ is the wronskian of the two solutions and is a constant, having no dependence on x or x_0. Using the above results in the expression for k_I^{-1}, we find

$$k_I^{-1}=\frac{\exp[V(x)/k_B T]}{(k_0 N)}\left[\frac{\partial}{\partial s}(Y(x_0,s)/Y(x_s,s))\right]_{s=0}, \tag{C7}$$

where $Y(x,s)=\exp[V(x)/(2k_B T)]y_1(x,s)$. As we know the equation obeyed by $y_1(x,s)$ we find the differential equation obeyed by $Y(x,s)$ to be

$$\left(s-A\exp[V(x)/(k_B T)]\frac{\mathrm{d}}{\mathrm{d}x}\exp[-V(x)/(k_B T)]\frac{\mathrm{d}}{\mathrm{d}x}\right)Y(x,s)=0 \tag{C8}$$

with the condition that $\mathrm{epx}[-V(x)/(2k_B T)]\ Y(x,s)\to 0$ as $x\to-\infty$ for any s. We note that, because of this, $\exp[V(x)/(2k_B T)]\partial Y(x,s)/\partial s\to 0$ in the same limit. Further, we also find that $Y(x,0)=$ *constant* which we denote by Y_0. Differentiating (C8) with respect to s partially and then putting $s=0$ gives

$$\frac{d}{dx}\exp[-V(x)/(k_B T)]\frac{d}{dx}\left(\frac{\partial Y(x,s)}{\partial s}\right)_{s=0} = \exp[-V(x)/(k_B T)]\ Y_0/A. \quad \text{(C9)}$$

One can now integrate (C9) (subject to $\exp[V(x)/(2k_B T)](\partial Y(x,s)/\partial s)_{s=0}\to 0$ as $x\to-\infty$. Then

$$\left(\frac{\partial Y(x,s)}{\partial s}\right)_{s=0}\Big/ Y_0 = \int^{x} dx_1 \exp[V(x_1)/(k_B T)]\int_{-\infty}^{x_1} dx_2 \exp[-V(x_2)/(k_B T)]/A. \quad \text{(C10)}$$

Carrying out the differentiation with respect to s in (C7) and remembering that $Y(x,0)=Y_0$, which is a constant independent of x, and using (C10), we get

$$k_I = \frac{\exp[V(x_s)/(k_B T)]}{(k_0 N)} + \int_{x0}^{x_s} dx_1 \exp[V(x_1)/(k_B T)] \int_{-\infty}^{x_1} dx_2 \exp[-V(x_2)/(k_B T)]/A. \quad \text{(C11)}$$

The second term in the above equation is just the quantity that one would obtain from a mean first passage approach (see Poornimadevi and Bagchi 1988). Our equation (29) follows on putting $V(x)=\mu\omega^2 x^2/2$ in the equation above.

References

Bagchi B 1987a *J. Chem. Phys.* **87** 5393
Bagchi B 1987b *Chem. Phys. Lett.* **138** 315
Bagchi B and Fleming G R 1990 *J. Phys. Chem.* **94** 9
Bagchi B, Fleming G R and Oxtoby D W 1983 *J. Chem. Phys.* **78** 7375
Chakravarti N and Sebastian K L 1993 *Chem. Phys. Lett.* **204** 4961
Courant R and Hilbert D 1953 *Methods of mathematical physics* (New York: Interscience) vol. 1, p. 351
Erdélyi A (ed.) 1953 *Higher transcendental function,* (New York: McGraw Hill) vol. 2, p. 115
Lippert E, Rettig W, Bonačič-Koutecky V, Heisel F and Miehé J A 1987 *Adv. Chem. Phys.* LXVIII, 1
Magnus W, Obserhettinger F and Soni R P 1966 Formulae and Theorems of Mathematical Physics, Springer Verlag, New York
Oster G and Nishijima N 1956 *J. Am. Chem. Soc.* **78** 1581
Poornimadevi C S and Bagchi B 1988 *Chem. Phys. Lett.* **149** 411
Schulten K, Schulten Z and Szabo A 1980 *Physica* **A100** 599
Sebastian K L 1992 *Phys. Rev.* **46** 1732
Sumi H and Marcus R A 1986 *J. Chem. Phys.* **84** 4894
Whittaker E T and Watson G N 1962 *A course on moderns analysis,* (Cambridge: University Press)