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A Simple Method for Calculating Diffusional Recombination Probabilities

JAN EMIL LARSEN AND J. BOIDEN PEDERSEN

Fysisk Institut, Odense Universitet, DK-5230 Odense M, Denmark

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We present a numerical method for calculating the diffusion-controlled recombination probability of a pair of interacting particles in an isotropic medium with scavengers. The method is finite and has a controllable accuracy. The algorithm is remarkably simple and can be implemented on a programmable pocket calculator.

1. INTRODUCTION

A fundamental quantity arising in the mathematical description of diffusional recombination phenomena in physical systems is the probability of recombination $\tilde{R}(s, r)$, i.e., the probability that two particles initially separated by a distance r will ever recombine in a medium with a uniform distribution of scavengers (which act as irreversible sinks), present in a concentration proportional to s. Alternatively $\tilde{R}(s, r)$ may be interpreted as the Laplace transform of the rate of recombination $R(t, r)$ in a medium free of scavengers.

It is generally not possible to solve the relevant equations by means of exact analytical methods. Various approximate and asymptotic solutions have been derived [1]. However, the validity of these approximate solutions for arbitrary values of r and s can only be tested by an accurate numerical method, which has been lacking. We present a simple, yet accurate method, which is both controllable in accuracy and faster than evaluating some of the more complicated approximate expressions for $\tilde{R}(s, r)$.

2. BASIC EQUATIONS

When the recombination is restricted to occur on a surface, then the recombination probability $\tilde{R}(s, r)$ satisfies the differential equation

$$[\nabla \cdot \mathbf{D}(\bar{r}) \cdot (\nabla + \nabla V) - k_s c_s]\, \tilde{R} = 0, \tag{1}$$

where V is the potential interactin between the particles in units of kT, $\mathbf{D}(\bar{r})$ is the relative diffusion tensor, k_s is the second-order scavenging rate constant, and c_s is the

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concentration of the scavenger. For an $(n+1)$-dimensional spherical symmetric system, Eq. (1) may be written as

$$\frac{d^2\tilde{R}}{dr^2}+\frac{d\tilde{R}}{dr}\left(\frac{n}{r}-\frac{dV}{dr}+\frac{d\ln D}{dr}\right)-\frac{k_s c_s}{D(r)}\tilde{R}=0 \tag{2}$$

by noting that $D(r)$ is positive definite. Equations (1) and (2) are straightforward generalizations of the equations which have recently appeared [2] and which are based on the adjoint (backward) Smoluchowski equation.

The recombination process is described by a boundary condition for $\tilde{R}(s,d)$ at $r=d$, the distance of closest approach. Only the diffusion controlled limit needs to be considered. The boundary conditions are

$$\tilde{R}(s,d)=1, \qquad \tilde{R}(s,r\to\infty)=0 \tag{3}$$

for $k_s c_s \neq 0$, which is the only case of interest since the $k_s c_s = 0$ results can be given in closed form. The partially diffusion controlled quantities are easily derived from the diffusion controlled quantities $\tilde{R}(s,r)$ and $(d\tilde{R}(s,r)/dr)_{r=d}$ as discussed previously [3].

As the domain of r in Eq. (2) is $[d,\infty]$, i.e., *semi-infinite*, it is convenient to make a change of the independent variable by means of an isomorphism $z=z(r)$ with $J=|dz/dr|$ being nonzero in the interior of the domain of r. We assume that $z(r)$ can be chosen such that the domain of z becomes $[0,1]$, with 1 representing the distance of the closest approach.

If we let l be a typical length and introduce the dimensionless quantities

$$w(z)=\frac{D(l)\,J(l)^2}{D(r)\,J(r)^2}, \tag{4}$$

$$g(z)=\left[\frac{D(r)\,r^n J(r)\exp(-V(r))}{D(l)\,l^n J(l)\exp(-V(l))}\right]^{1/2}, \tag{5}$$

$$s=k_s c_s/D(l)\,J(l)^2, \tag{6}$$

then Eq. (2) may be written in the convenient form

$$\frac{d^2\tilde{R}}{dz^2}+\frac{2}{g}\frac{dg}{dz}\frac{d\tilde{R}}{dz}-sw\tilde{R}=0. \tag{7}$$

Another useful form of this equation is

$$\frac{d^2(g\tilde{R})}{dz^2}-\frac{(g\tilde{R})}{g}\frac{d^2g}{dz^2}-sw(g\tilde{R})=0. \tag{8}$$

The boundary values for $\tilde{R}$ with z as argument are

$$\tilde{R}(s,1)=1, \qquad \tilde{R}(s,0)=0. \tag{9}$$

When $\tilde{R}(s, z)$ is considered the Laplace transform of the rate of recombination $R(\tau, z)$, then a dimensionless time τ is implied,

$$\tau = D(l)\, J(l)^2\, t. \tag{10}$$

3. Numerical Method

Any numerical method is bound to discretize the equation in some appropriate manner. It is essential that this discretization is well balanced with respect to where and how many discretization points to place. From a numerical point of view, it is most convenient that the independent variable is discretized with equidistant points. Furthermore, it is necessary that the domain of discretization is finite, as an infinite domain cannot be covered with a finite number of points. This can be accomplished by choosing $z(r)$ such that the domain of z becomes finite. The choice of $z(r)$ can be made such that a uniform distribution of points in z-space corresponds to a distribution in r-space reflecting "the relative importance of the points. Ideally (at least for small values of s) z could be chosen such that $z(r) = \tilde{R}(0, r)$ that is

$$z(r) \propto \int^r \frac{e^V x^{-n}}{D}\, dx \tag{11}$$

which makes g constant. However, for numerical purposes it is more convenient to choose another and simpler form of $z(r)$.

On ends up with a second-order two-point boundary value problem

$$Mu = 0, \qquad u(0, s) = 0, \qquad u(1, s) = 1, \tag{12}$$

where M is a second-order differential operator given by Eq. (7) or (8) and u is $\tilde{R}$ or $g\tilde{R}$, respectively.

One of the standard methods for solving this kind of boundary value problems is the shooting method [4], which has in fact been used for the present problem [5], but without the introduction of the transformation $z(r)$. In this method one solves the corresponding initial value problem with $u(0) = 0$, $u'(0) = \gamma$, and adjusts γ until the solution satisfies $u(1) = 1$. There are, however, several drawbacks with this method. It is iterative, and thus in principle not finite. A more serious drawback is that the initial value problem may become stiff, meaning that very small stepsizes are necessary. This can be the case in the present problem because of singularities at the endpoints.

Contrary to Eq. (2), Eqs. (7) and (8) permit the use of the standard finite difference method [4] which gives rise to a finite algorithm with a controllable accuracy. The interval [0, 1] is divided into N pieces, each of length $\Delta z = 1/N$, and the function $u(s, z)$ is represented as a vector $u_j = u(s, z_j)$ with $z_j = j\,\Delta z$. The second-order differential operator M is represented by a tridiagonal matrix M using the finite difference approximations

$$\left.\frac{du}{dz}\right|_{z_j} \simeq \frac{u_{j+1}-u_{j-1}}{2\Delta z}$$

and

$$\left.\frac{d^2u}{dz^2}\right|_{z_j} \simeq \frac{u_{j+1}-2u_j+u_{j-1}}{\Delta z^2}$$

which, because of the uniform distribution, is correct to $O(\Delta z^2)$. With this discretization, the equations to solve are

$$\begin{aligned} u_0 &= 0, \\ M_j^- u_{j-1} + M_j^0 u_j + M_j^+ u_{j+1} &= 0, \\ u_N &= 1. \end{aligned} \tag{13}$$

If g is nonzero in the domain of z, analytically as well as with respect to an accurate numerical representation, then Eq. (8) with $u = g\tilde{R}/g(1)$ may be used, giving

$$\begin{aligned} \Delta z^2 M_j^0 &= -2 - \left.\frac{1}{g}\frac{d^2g}{dz^2}\right|_{z_j} - sw_j \simeq -\frac{g_{j-1}+g_{j+1}}{g_j} - sw_j, \\ \Delta z^2 M_j^{\pm} &= 1. \end{aligned} \tag{14}$$

If $g(1)$ is zero or infinite, at least in a numerical sense, then Eq. (7) with $u = \tilde{R}$ must be used, giving

$$\begin{aligned} \Delta z^2 M_j^0 &= -2 - sw_j, \\ \Delta z^2 M_j^{\pm} &= 1 \pm 2\left(\frac{g'}{g}\right)_{z_j} \Delta z \simeq 1 \pm \frac{g_{j+1}-g_{j-1}}{g_j}. \end{aligned} \tag{15}$$

From the definition of g one observes that when d becomes very small or $|V|$ becomes very large Eq. (15) should be used with g'/g given explicitly, if possible, or, otherwise, approximately as indicated. Apart from such pathological cases one further notes that all the necessary information is contained in g. As g is closely related to a measureable pair-correlation function, this is an extra avantage for calculation of $\tilde{R}$ based on experimental results.

4. ALGORITHM

Equation (13) may be elegantly solved by a standard method for tridiagonal systems [6]. Define α_j's, such that

$$u_j = \alpha_{j+1} u_{j+1}, \qquad j = 0, \ldots, N \tag{16}$$

with $\alpha_1 = 0$ determined by the boundary condition $u_0 = 0$. By insertion into Eq. (13) the following consistent recursion relations are found:

$$\alpha_1 = 0, \tag{17}$$

$$\alpha_{j+1} = -\frac{M_j^+}{M_j^0 + \alpha_j M_j^-}, \tag{18}$$

and

$$u_N = 1, \tag{19}$$

$$u_j = \alpha_{j+1} u_{j+1}. \tag{20}$$

This algorithm is finite, with the number of operations to perform proportional to N. Notice that because of the recursion relations, only one value of α and u need to be stored at any time. Thus the storage requirement is very small; in fact, it is possible to program the algorithm on a programmable pocket calculator.

Because of the uniform distribution of points the accuracy of the results can be found by use of Richardson extrapolation (deferred approach to the limit) [4]: If $u_j(\Delta z)$ denotes the solution obtained with discretization $\Delta z = 1/N$, and $u_j(0)$ the exact solution, then the error

$$E(j) = u_j(\Delta z) - u_j(0) = c_1 \Delta z + c_2 \Delta z^2 + c_3 \Delta z^3 + \cdots.$$

It is well known [4] that, under weak assumptions on u, the $O(\Delta z^2)$-discretization chosen makes any odd-ordered coefficient c_i equal to zero. If it is assumed that $c_2 \Delta z^2 \ll c_4 \Delta z^4$ in the limit of small Δz, then c_2 may be determined as

$$c_2(j) = \frac{u_j(2\,\Delta z) - u_j(\Delta z)}{3\;\Delta z^2} \tag{21}$$

thus estimating the error as

$$E(j) = \tfrac{1}{3}(u_j(2\,\Delta z) - u_j(\Delta z)) \tag{22}$$

and using

$$\hat{u}_j = u_j(\Delta z) - E(j) \tag{23}$$

as an improved value of u, correct to $O(\Delta z^4)$. This process is continued until an acceptable small error is obtained.

5. Test of Method

In order to illustrate and test the method on an example of physical interest we have chosen a three-dimensional system with a Coulomb potential, with a constant diffusion coefficient, and with a distance of closest approach equal to zero. The equation to solve is obtained from Eq. (7),

$$\frac{d^2\tilde{R}}{dz^2}+\frac{2z-1}{(1-z)^2}\frac{d\tilde{R}}{dz}-sz^{-4}\tilde{R}=0, \tag{24}$$

where we have chosen $z = 1/(1+x)$, and x is the separation measured in units of the Onsager length $r_c = q_1q_2/\varepsilon kT$, i.e., $V(x) = -1/x$.

We have solved Eq. (24) with sets of different discretizations of the form N, $2N$, and $4N$ and monitored the second- and fourth-order errors

$$E_2 = c_2\Delta z^2, \qquad E_4 = c_4\Delta z^4 \tag{25}$$

for $z = 0.5$ as a function of N, see Fig. 1. In all cases we found that E_2 is proportional to N^{-2}, and that E_4 is largely proportional to N^{-4}, meaning that c_2 and c_4 are independent of N, thus justifying the use of the Richardson extrapolation. The deviation of E_4 from an N^{-4}-proportionality is a result of numerical round-off and cancellation errors and to the effect of higher order error terms (E_6, E_8, etc.), which could be separated by further extrapolation.

Notice that the benefits of the extrapolation exceed its cost. Calculations with N and $2N$ points and elimination of the second-order error involve the same number of operations as a single calculation with $3N$ points, while the accuracy is comparable to or better than is obtained with $4N$ points.

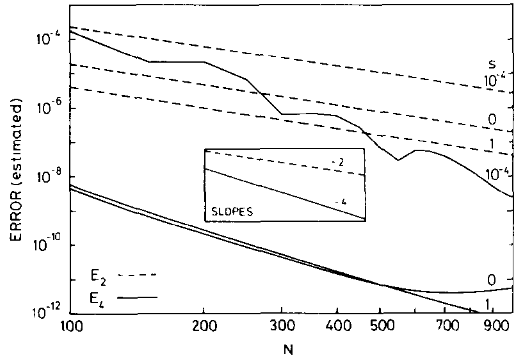

FIG. 1. Second- and fourth-order errors (E_2 and E_4) as a function of the numbers of discretization points (N), for three selected values of s. The calculations were performed for a three-dimensional system with an attractive Coulomb potential, a distance of closest approach equal to zero, and $z = 0.5$ (i.e., $x = 1$). The insert displays lines with slopes of −2 and −4 for comparison.

6. DISCUSSION

We have presented a numerical method which can be used to solve the boundary value problem for $\tilde{R}(s, r)$. The method is very simple and easy to program, and it is possible to control the error in an efficient way.

Abell *et al.* [5] have published a method based on the shooting method. As with any shooting method, they have to find the solution by solving the initial value problem several times to locate the shooting parameter γ, such that the boundary conditions are fulfilled. Based on an inequality they can control the accuracy of the result by giving bounds to γ. Notice, however, that this does not directly measure the error of the function as this is not only determined by the accuracy of γ but on the method used to solve the initial value problem as well. Because of the possible stiffness of the initial value problem it may turn out that for practical purposes it is not possible to solve the initial value problem with a constant stepsize, in which case the Richardson extrapolation cannot be used. Finally, they solve the boundary value problem in an infinite domain.

The recombination probability could alternatively be calculated by using a variable stepsize in r [7]; however, the accuracy of such a calculation is not readily controllable, the Richardson estrapolation cannot be used, and the computational demands are significantly larger.

The essential step in the present method is the introduction of a suitable transformation $z(r)$ which reflects the physical problem and which has a finite domain.

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