Computer Physics Communications 198 (2016) 41–46

Contents lists available at ScienceDirect

Computer Physics Communications

journal homepage: www.elsevier.com/locate/cpc

Calculation of the second term of the exact Green's function of the diffusion equation for diffusion-controlled chemical reactions

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ARTICLE INFO

Article history:
Received 4 February 2015
Accepted 3 September 2015
Available online 25 September 2015

Keywords:
Green's function of the diffusion equation
Diffusion-controlled chemical reactions
Radiation chemistry
Bessel functions
Analytical integration

ABSTRACT

The exact Green's function of the diffusion equation (GFDE) is often considered to be the gold standard for the simulation of partially diffusion-controlled reactions. As the GFDE with angular dependency is quite complex, the radial GFDE is more often used. Indeed, the exact GFDE is expressed as a Legendre expansion, the coefficients of which are given in terms of an integral comprising Bessel functions. This integral does not seem to have been evaluated analytically in existing literature. While the integral can be evaluated numerically, the Bessel functions make the integral oscillate and convergence is difficult to obtain. Therefore it would be of great interest to evaluate the integral analytically. The first term was evaluated previously, and was found to be equal to the radial GFDE. In this work, the second term of this expansion was evaluated. As this work has shown that the first two terms of the Legendre polynomial expansion can be calculated analytically, it raises the question of the possibility that an analytical solution exists for the other terms.

1. Introduction

1.1. The Green's function of the diffusion equation for partially diffusion-controlled chemical reactions

The exact Green's function of the diffusion equation (GFDE) for interparticle diffusion is used as the gold standard to validate chemical theories [1,2] and, therefore, is of great importance for radiation chemistry codes [3]. The GFDE is used in the chemistry code included in the software RITRACKS [4] as a probability distribution for a particle initially located at position (r_0, θ_0, ϕ_0) in a spherical coordinate system, to be located at position (r, θ, ϕ) at time t. The GFDE is considered exact for a 2-particle system. This GFDE is given by [5,6]

$$p_{\text{ex}}(r, \theta, \phi, t|r_0, \theta_0, \phi_0) = \frac{1}{4\pi\sqrt{rr_0}} \sum_{n=0}^{\infty} (2n+1) P_n(\cos\gamma) \int_0^{\infty} e^{-u^2 Dt} u F_{n+1/2}(u, r) F_{n+1/2}(u, r_0) du, \tag{1}$$

where D is the sum of the diffusion coefficients of the reacting particles, $P_n(x)$ are the Legendre polynomials, and

$$F_{\upsilon}(u, r) = \frac{(2\sigma k_a + 1)\left[J_{\upsilon}(ur)Y_{\upsilon}(u\sigma) - Y_{\upsilon}(ur)J_{\upsilon}(u\sigma)\right] - 2u\sigma\left[J_{\upsilon}(ur)Y'_{\upsilon}(u\sigma) - Y_{\upsilon}(ur)J'_{\upsilon}(u\sigma)\right]}{\sqrt{\left[(2\sigma k_a + 1)J_{\upsilon}(u\sigma) - 2u\sigma J'_{\upsilon}(u\sigma)\right]^2 + \left[(2\sigma k_a + 1)Y_{\upsilon}(u\sigma) - 2u\sigma Y'_{\upsilon}(u\sigma)\right]^2}}. \tag{2}$$

In the latter equation, $J_{\upsilon}(z)$ and $Y_{\upsilon}(z)$ are Bessel functions [7]; σ is the reaction radius; k_a is the reaction rate constant; r_0 and r are the interparticle distances at times 0 and t; and

$$\cos(\gamma) = \cos(\theta)\cos(\theta_0) + \sin(\theta)\sin(\theta_0)\cos(\phi - \phi_0). \tag{3}$$

In Eq. (3), θ_0 and ϕ_0 are the interparticle vector angles at the initial time, and θ and ϕ are the corresponding angles at time t, and γ is the angle between the initial and final interparticle vectors.

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http://dx.doi.org/10.1016/j.cpc.2015.09.001

1.2. Particular cases

For free diffusion ($k_a = 0, \sigma \to 0$), $F_{n+1/2}(u, r) \to J_{n+1/2}(ur)$, so that the integral in Eq. (1) can be evaluated directly:

$$p_{fr}(r, \theta, \phi, t|r_0, \theta_0, \phi_0) = \frac{1}{4\pi\sqrt{rr_0}} \sum_{n=0}^{\infty}(2n+1)P_n(\cos\gamma)\frac{1}{2Dt}\exp\left(-\frac{r^2+r_0^2}{4Dt}\right) I_{n+1/2}\left(\frac{rr_0}{2Dt}\right). \tag{4}$$

Using the identity [7]

$$\exp(z\cos\gamma) = \sqrt{\frac{\pi}{2z}} \sum_{n=0}^{\infty}(2n+1)P_n(\cos\gamma)I_{n+1/2}(z), \tag{5}$$

Eq. (4) can be rewritten

$$p_{fr}(r, \theta, \phi, t|r_0, \theta_0, \phi_0) = \frac{1}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2+r_0^2-2rr_0\cos\gamma}{4Dt}\right). \tag{6}$$

This is indeed the GFDE for free diffusion.

In a previous publication [8], the integral present in Eq. (1) was calculated for $n = 0$ and $k_a \geq 0$. The result is given by

$$\int_0^{\infty} e^{-u^2Dt}uF_{1/2}(u, r)F_{1/2}(u, r_0)du = \frac{1}{\sqrt{(rr_0)}}\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right] + \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\} + \alpha\frac{1}{\sqrt{(rr_0)}}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}, \alpha\sqrt{Dt}\right), \tag{7}$$

where $W(x, y) = \exp(2xy + y^2)Erfc(x + y)$, and $\alpha = (k_a\sigma + 1)/(\sigma)$. Interestingly, this corresponds to the radial Green's function. For $k_a \to \infty$, note that

$$\lim_{k_a\to\infty}\int_0^{\infty} e^{-u^2Dt}uF_{1/2}(u, r)F_{1/2}(u, r_0)du = \frac{1}{\sqrt{(rr_0)}}\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right] - \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\}. \tag{8}$$

The complex integral that appears in Eq. (1) does not seem to have been evaluated in the existing literature. In this paper, the integral is calculated directly for the second term ($n = 1$) of diffusion-controlled reactions ($k_a \to \infty$). Possible strategies to evaluate this integral for other values of n are discussed.

2. Calculation of the second term for $k_a \to \infty$

In this section, the second term of the expansion given in Eq. (1), i.e. for $n = 1$, is calculated. A numerical verification of each step is performed in the accompanying Mathematica document (see supplementary data, Appendix A). At this time it was only possible to calculate the integral for $k_a \to \infty$. The integral to evaluate is

$$I = \int_0^{\infty} e^{-u^2Dt}uF_{3/2}(u, r)F_{3/2}(u, r_0)du. \tag{9}$$

Using the definition of the Bessel functions, and the limit $k_a \to \infty$, the integral in Eq. (9) can be expressed with trigonometric functions:

$$I = \int_0^{\infty} e^{-u^2Dt}u\left[2\frac{u(\sigma-r)\cos[u(r-\sigma)] + (1+r\sigma u^2)\sin[u(r-\sigma)])(u(\sigma-r_0)\cos[u(r_0-\sigma)] + (1+r_0\sigma u^2)\sin[u(r_0-\sigma)])}{(rr_0)^{3/2}\pi u^3(1+u^2\sigma^2)}\right]du. \tag{10}$$

2.1. Separation of the integral into integrable terms

Using basic trigonometric identities, the integral can be rewritten as the sum of four terms:

$$p_1 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\frac{(1+rr_0u^2)\cos[u(r-r_0)]}{u^3}du. \tag{11a}$$

$$p_2 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\frac{(-1+u^2(rr_0-2(r+r_0)\sigma+\sigma^2)-rr_0u^4\sigma^2)\cos[u(r+r_0-2\sigma])}{u^3(1+u^2\sigma^2)}du. \tag{11b}$$

$$p_3 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\frac{u(r-r_0)\sin[u(r-r_0)]}{u^3}du. \tag{11c}$$

$$p_4 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\left[u\frac{(-(r+r_0-2\sigma)+u^2(-2rr_0\sigma+(r+r_0)\sigma^2))\sin[u(r+r_0-2\sigma)]}{u^3(1+u^2\sigma^2)}\right]du. \tag{11d}$$

Only p_3 can be integrated directly. Therefore, it is necessary to further split p_1, p_2 and p_4. As the term p_1 is not integrable, it needs to be split into three parts so the non-integrable part can be combined with another term:

$$p_{1a} = \frac{1}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} u \frac{\cos[u(r-r_0)]}{u^3(1+u^2\sigma^2)} du. \tag{12a}$$

$$p_{1b} = \frac{\sigma^2}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \frac{\cos[u(r-r_0)]}{(1+u^2\sigma^2)} du. \tag{12b}$$

$$p_{1c} = \frac{rr_0}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \cos[u(r-r_0)] du. \tag{12c}$$

The term p_2 is also split into three parts:

$$p_{2a} = -\frac{rr_0}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \cos[u(r+r_0-2\sigma)] du. \tag{13a}$$

$$p_{2b} = \frac{2rr_0 - 2(r+r_0)\sigma + \sigma^2}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \frac{\cos[u(r+r_0-2\sigma)]}{(1+u^2\sigma^2)} du. \tag{13b}$$

$$p_{2c} = -\frac{1}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} u \frac{\cos[u(r+r_0-2\sigma)]}{u^3(1+u^2\sigma^2)} du. \tag{13c}$$

The term p_4 is split into four parts:

$$p_{4a} = \frac{(r+r_0)}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \frac{\sin[u(r+r_0-2\sigma)]}{u} du. \tag{14a}$$

$$p_{4b} = -\frac{2rr_0\sigma}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} u \frac{\sin[u(r+r_0-2\sigma)]}{(1+u^2\sigma^2)} du. \tag{14b}$$

$$p_{4c} = -\frac{2(r+r_0-\sigma)}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} u \frac{\sin[u(r+r_0-2\sigma)]}{u^2} du. \tag{14c}$$

$$p_{4d} = \frac{2(r+r_0-\sigma)\sigma^2}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} u \frac{\sin[u(r+r_0-2\sigma)]}{(1+u^2\sigma^2)} du. \tag{14d}$$

2.2. *Integration of the terms separately*

The first term p_{1a} is not integrable. It will be dealt with later in this work.

In Erdelyi's *Tables of Integral Transforms*, vol. 1, p. 15 [9] (or Gradshteyn and Ryzhik, p. 530 [10]), we find that

$$\int_0^\infty e^{-\alpha x^2} \frac{\cos(x\gamma)}{x^2+\beta^2} dx = \frac{\pi}{4\beta} e^{\alpha\beta^2} \left[e^{-\beta\gamma} Erfc\left(\frac{2\alpha\beta-\gamma}{2\sqrt{\alpha}}\right) + e^{\beta\gamma} Erfc\left(\frac{2\alpha\beta+\gamma}{2\sqrt{\alpha}}\right)\right], \tag{15}$$

so that p_{1b} can be evaluated:

$$p_{1b} = \frac{\sigma}{4(rr_0)^{3/2}} e^{Dt/\sigma^2} \left[e^{-(r-r_0)/\sigma} Erfc\left(\frac{2Dt-(r-r_0)\sigma}{2\sigma\sqrt{Dt}}\right) + e^{(r-\sigma)/\sigma} Erfc\left(\frac{2Dt+(r-r_0)\sigma}{2\sigma\sqrt{Dt}}\right)\right]. \tag{16}$$

In Gradshteyn and Ryzhik, p. 515 [10] we find that

$$\int_0^\infty e^{-\alpha x^2} \cos(\beta x) dx = \sqrt{\frac{\pi}{4\alpha}} \exp\left(-\frac{\beta^2}{4\alpha}\right), \tag{17}$$

so that p_{1c} can be evaluated:

$$p_{1c} = \frac{rr_0}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \cos[u(r-r_0)] du = \frac{1}{\sqrt{4\pi rr_0 Dt}} \exp\left[-\frac{(r-r_0)^2}{4Dt}\right]. \tag{18}$$

Similarly,

$$p_{2a} = -\frac{rr_0}{\pi (rr_0)^{3/2}} \int_0^\infty e^{-u^2Dt} \cos[u(r+r_0-2\sigma)] du = -\frac{1}{\sqrt{4\pi rr_0 Dt}} \exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]. \tag{19}$$

The term p_{2b} can also be evaluated using Eq. (15):

$$p_{2b} = \frac{2rr_0 - 2(r+r_0)\sigma + \sigma^2}{4(rr_0)^{3/2}\sigma} e^{Dt/\sigma^2} \left[e^{-(r+r_0-2\sigma)/\sigma} Erfc\left(\frac{2Dt-(r+r_0-2\sigma)\sigma}{2\sigma\sqrt{Dt}}\right) + e^{(r+r_0-2\sigma)/\sigma} Erfc\left(\frac{2Dt+(r+r_0-2\sigma)\sigma}{2\sigma\sqrt{Dt}}\right)\right]. \tag{20}$$

The term p_{2c} is not integrable. It will be dealt with later.

In Gradshteyn and Ryzhik p. 529 [10] we find that

$$\int_0^\infty e^{-\alpha x^2}\frac{\sin(\beta x)}{x}dx = \frac{\pi}{2}Erf\left[\frac{\beta}{2\sqrt{\alpha}}\right], \tag{21}$$

so that p_3 can be evaluated:

$$p_3 = \frac{r-r_0}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}u\frac{\sin[u(r-r_0)]}{u^2}du = \frac{r-r_0}{2(rr_0)^{3/2}}Erf\left[\frac{r-r_0}{\sqrt{4Dt}}\right]. \tag{22}$$

The term p_{4a} can be evaluated similarly:

$$p_{4a} = \frac{r+r_0}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\sin[u(r+r_0-2\sigma)]}{u}du = \frac{r+r_0}{2(rr_0)^{3/2}}Erf\left[\frac{r+r_0-2\sigma}{\sqrt{4Dt}}\right]. \tag{23}$$

In Erdelyi's *Tables of Integral Transforms*, vol. 1, p. 74 [9] (or Gradshteyn and Ryzhik, p. 530 [10]), we find that

$$\int_0^\infty e^{-\alpha x^2}x\frac{\sin(x\gamma)}{x^2+\beta^2}dx = \frac{\pi}{4}e^{\alpha\beta^2}\left[e^{-\beta\gamma}Erfc\left(\frac{2\alpha\beta-\gamma}{2\sqrt{\alpha}}\right) - e^{\beta\gamma}Erfc\left(\frac{2\alpha\beta+\gamma}{2\sqrt{\alpha}}\right)\right], \tag{24}$$

so that

$$p_{4b} = -\frac{rr_0}{2\sigma(rr_0)^{3/2}}e^{Dt/\sigma^2}\left[e^{-(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt-\sigma(r+r_0-2\sigma)}{2\sigma\sqrt{Dt}}\right) - e^{(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt+\sigma(r+r_0-2\sigma)}{2\sigma\sqrt{Dt}}\right)\right]. \tag{25}$$

The term p_{4c} is in the form given by Eq. (21):

$$p_{4c} = -\frac{(r+r_0-\sigma)}{(rr_0)^{3/2}}Erf\left[\frac{r+r_0-2\sigma}{2\sqrt{Dt}}\right]. \tag{26}$$

The term p_{4d} is in the form given by Eq. (24), so that

$$p_{4d} = \frac{(r+r_0-\sigma)}{2(rr_0)^{3/2}}e^{Dt/\sigma^2}\left[e^{-(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt-\sigma(r+r_0-2\sigma)}{2\sigma\sqrt{Dt}}\right) - e^{(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt+\sigma(r+r_0-2\sigma)}{2\sigma\sqrt{Dt}}\right)\right]. \tag{27}$$

The terms p_{1a} and p_{2c} are not integrable separately. However, their sum can be integrated by using decomposition into partial fractions:

$$\frac{1}{u^2(1/\sigma^2+u^2)} \equiv \sigma^2\left(\frac{1}{u^2} - \frac{1}{1/\sigma^2+u^2}\right). \tag{28}$$

Using this identity, we can write

$$p_{1a} = \frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\cos[u(r-r_0)]}{u^2}du - \frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\cos[u(r-r_0)]}{u^2+1/\sigma^2}du. \tag{29a}$$

$$p_{2c} = -\frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\cos[u(r+r_0-2\sigma)]}{u^2}du + \frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\cos[u(r+r_0-2\sigma)]}{u^2+1/\sigma^2}du. \tag{29b}$$

Two integrals are of the form given by Eq. (15). The first two parts can be combined using trigonometric identities:

$$\frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{2\sin[u(r-\sigma)]\sin[u(r_0-\sigma)]}{u^2}du. \tag{30}$$

This integral can be integrated directly by Mathematica. The result is

$$\frac{1}{2(rr_0)^{3/2}}\left[2\sqrt{Dt}\left(\frac{e^{-(r+r_0-2\sigma)^2/4Dt}-e^{-(r-r_0)^2/4Dt}}{\sqrt{\pi}}\right) + (r_0-r)Erf\left(\frac{r-r_0}{\sqrt{4Dt}}\right) + (r+r_0-2\sigma)Erf\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}}\right)\right]. \tag{31}$$

The result of the second part of p_{1a} is

$$-\frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\cos[u(r-r_0)]}{u^2+1/\sigma^2}du = -\frac{1}{\pi(rr_0)^{3/2}}\frac{\pi}{4(1/\sigma)}e^{Dt/\sigma^2}\left[e^{-(r-r_0)/\sigma}Erfc\left(\frac{2Dt/\sigma-(r-r_0)}{2\sqrt{Dt}}\right) + e^{(r-r_0)/\sigma}Erfc\left(\frac{2Dt/\sigma+(r-r_0)}{2\sqrt{Dt}}\right)\right]. \tag{32}$$

Similarly,

$$\frac{1}{\pi(rr_0)^{3/2}}\int_0^\infty e^{-u^2Dt}\frac{\cos[u(r+r_0-2\sigma)]}{u^2+1/\sigma^2}du = \frac{1}{\pi(rr_0)^{3/2}}\frac{\pi}{4(1/\sigma)}e^{Dt/\sigma^2}\left[e^{-(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt/\sigma-(r+r_0-2\sigma)}{2\sqrt{Dt}}\right) + e^{(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt/\sigma+(r+r_0-2\sigma)}{2\sqrt{Dt}}\right)\right]. \tag{33}$$

2.3. Calculating the final result

Now that all parts have been integrated, the final result can be calculated. After simplifications, the final result is

$$I=\int_0^\infty e^{-u^2Dt}uF_{3/2}(u,r)F_{3/2}(u,r_0)du=\frac{2Dt-rr_0}{2(rr_0)^{3/2}\sqrt{\pi Dt}}\left(\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]-\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]\right)$$
$$+\frac{(r-\sigma)(r_0-\sigma)}{(rr_0)^{3/2}\sigma}e^{Dt/\sigma^2}\left[e^{(r+r_0-2\sigma)/\sigma}Erfc\left(\frac{2Dt+\sigma(r+r_0-2\sigma)}{2\sigma\sqrt{Dt}}\right)\right]. \quad (34)$$

It may also be expressed using the function W defined previously:

$$I=\int_0^\infty e^{-u^2Dt}uF_{3/2}(u,r)F_{3/2}(u,r_0)du=\frac{2Dt-rr_0}{2(rr_0)^{3/2}\sqrt{\pi Dt}}\left(\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]-\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]\right)$$
$$+\frac{(r-\sigma)(r_0-\sigma)}{(rr_0)^{3/2}\sigma}W\left(\frac{r+r_0-2\sigma}{2\sqrt{Dt}},\frac{\sqrt{Dt}}{\sigma}\right). \quad (35)$$

2.4. Verification of the solution for the limiting case $\sigma\to 0$

The verification is done in the accompanying Mathematica document. Another verification can be done by looking at the limit case $\sigma\to 0$. We note that $Erfc(z)$ can be expressed as [8]:

$$\sqrt{\pi}ze^{z^2}Erfc(z)\sim 1+\sum_{m=1}^{\infty}(-1)^m\frac{1.3\ldots(2m-1)}{(2z^2)^m}. \quad (36)$$

Since $\sigma\to 0, z\to\infty$, the only significant term in (36) is the first. We get

$$\lim_{\sigma\to 0}\int_0^\infty e^{-u^2Dt}uF_{3/2}(u,r)F_{3/2}(u,r_0)du=\frac{2Dt-rr_0}{2(rr_0)^{3/2}\sqrt{\pi Dt}}\left(\exp\left[-\frac{(r+r_0)^2}{4Dt}\right]-\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]\right)$$
$$+\frac{(r-\sigma)(r_0-\sigma)}{(rr_0)^{3/2}\sigma}e^{Dt/\sigma^2}\left[e^{(r+r_0-2\sigma)/\sigma}\frac{2\sigma\sqrt{Dt}}{\sqrt{\pi}2Dt}\exp\left[-\left(\frac{2Dt+\sigma(r+r_0-2\sigma)}{2\sigma\sqrt{Dt}}\right)^2\right]\right] \quad (37)$$

which simplifies to

$$\lim_{\sigma\to 0}\int_0^\infty e^{-u^2Dt}uF_{3/2}(u,r)F_{3/2}(u,r_0)du=\frac{2Dt+rr_0}{2(rr_0)^{3/2}\sqrt{\pi Dt}}\exp\left[-\frac{(r+r_0)^2}{4Dt}\right]-\frac{2Dt-rr_0}{2(rr_0)^{3/2}\sqrt{\pi Dt}}\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]. \quad (38)$$

In this case the integral can be evaluated directly by Mathematica (supplementary data, Appendix A). The same result was found by Mathematica.

3. Discussion

This long mathematical calculation has led to an analytical solution. Despite the complexity of this integral, the result is relatively simple. The integrals can certainly be evaluated numerically, but the Bessel functions present in the integrand are difficult to evaluate because they oscillate and the integral converge slowly. Additionally, the integrand includes limits in the form (0/0), which may lead to computational errors. Solving integrals analytically does not follow the current trends in science, but that does not mean that this approach cannot produce an useful result. In fact it would be of great interest to solve the integral for the general case ($n>0$, $k_a>0$), because this Green's function could be calculated much more efficiently in radiation chemistry programs. Similar integrals have been evaluated by Titchmarsh [11] by using integration in the complex plane. This strategy would be quite interesting to use since the calculation necessitates evaluation of the integrand only in limiting cases, avoiding the need to deal with the Bessel functions directly.

Acknowledgments

The author would like to thank Dr. Erik Talvila (University of Fraser Valley) for his help in evaluating some integrals. The ongoing financial support of the National Aeronautics and Space Administration's Space Radiation Program Element (NASA contract number NAS9-02078) is gratefully acknowledged.

Appendix A. Supplementary data

An accompanying Mathematica 10.0.1 document with all details and verifications of the calculations done for this article can be found in the online version at http://dx.doi.org/10.1016/j.cpc.2015.09.001.

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