Quantum mechanical inspired factorization of the molecule pair propagator in theories of diffusion-influenced reactions

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Abstract
Building on mathematical similarities between quantum mechanics and theories of diffusion-influenced reactions, we discuss how the propagator of a reacting molecule pair can be represented as a product of three factors in the Laplace domain. This representation offers several advantages. First, the full propagator can be calculated without ever having to solve the corresponding partial differential equation or path integral. Second, the representation is quite general and capable of capturing not only the classical Smoluchowski-Collins-Kimball model, but also alternative theories, as is here exemplified by the case of a delta- and step-function potential in one and two dimensions, respectively. Third, the three factors correspond to physical quantities that feature prominently in stochastic spatially-resolved simulation algorithms and hence the interpretation of current and the design of future algorithms may benefit. Finally, the representation may serve as a suitable starting point for numerical approximations that could be employed to enhance the efficiency of stochastic simulations.

1 Introduction
Stochastic processes, like Brownian motion, and quantum phenomena can be described by mathematical structures that appear to be quite similar

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A case in point is the transition probability density function (PDF) \( p(x,t|x_0,t_0) \), a central quantity in the theory of Brownian motion that yields the probability to find a Brownian walker at \( x \) at time \( t \), provided it started at \( x_0 \) at \( t_0 < t \). The transition PDF can be calculated in terms of a path integral that may formally be written as

\[
 p(x,t|x_0,t_0) \sim \sum_{x(\tau):x_0 \to x} e^{-S_E[x(\tau)]},
\]

where the sum includes all paths \( x(\tau) \) that satisfy \( x(t_0) = x_0 \) and \( x(t) = x \). \( S_E[x(\tau)] \) denotes a certain functional of \( x(\tau) \). Quite analogously, the Feynmann transition amplitude \( K(x,t|x_0,t_0) \) is also given by a path integral

\[
 K(x,t|x_0,t_0) \sim \sum_{x(\tau):x_0 \to x} e^{i\frac{\hbar}{\epsilon}S[x(\tau)]},
\]

where \( S[x(\tau)] \) refers to the classical action functional. Although the physical context described by Eq. (1) is quite different from the one represented by Eq. (2), the path integrals can in general be transformed into each other by means of a Wick rotation \cite{21, 6, 22} and the functional \( S_E[x(\tau)] \) in Eq. (1) is the Euclidean version of the action \( S[x(\tau)] \).

Typically, path integrals come along with partial differential equations (PDE) and integral equations \cite{26}.

Hence, unsurprisingly, the formal correspondence continues on the level of the associated PDE. As is well-known, both the transition PDF \( p(x,t|x_0,t_0) \) and the Feynmann amplitude \( K(x,t|x_0,t_0) \) are the Green’s functions (GF) of the diffusion equation

\[
 \frac{\partial p(x,t|x_0)}{\partial t} = \left[ D \frac{\partial^2}{\partial x^2} + V(x) \right] p(x,t|x_0),
\]

\[
 p(x,t=0|x_0) = \delta(x-x_0),
\]

and the Schrödinger equation,

\[
 \frac{\partial K(x,t|x_0)}{\partial t} = \left[ \frac{i\hbar}{2m} \frac{\partial^2}{\partial x^2} - \frac{i}{\hbar} V(x) \right] K(x,t|x_0),
\]

\[
 K(x,t=0|x_0) = \delta(x-x_0),
\]

respectively.

In this manuscript, we exploit the fundamental relationship between quantum mechanics (QM) and Brownian motion in the context of theories of
diffusion-influenced reactions [12, 20]. In the classical Smoluchowski-Collins-Kimball (SCK) picture [25, 7, 12, 20], the diffusion-influenced reaction of an isolated pair of molecules is described by a diffusion equation (Eq. (3)) with vanishing potential $V(x)$. The actual reaction is instead implemented by imposing suitable boundary conditions (BC) at the so-called encounter radius [25, 7, 11, 3, 15, 17]. However, there is an alternative approach that abandons the BC and postulates a non-vanishing potential [27, 9, 10, 14, 2, 18, 19]. This formulation is not only capable of including the classical theory, but it may also serve as a starting point to construct more general theories of diffusion-influenced reactions. At the same time, its mathematical structure is closer to the formalism of QM and hence it may pave the way to borrow techniques from QM for theories of diffusion-influenced reactions.

The manuscript is structured as follows. First, we briefly describe the path decomposition expansion (PDX) that has been applied to the quantum mechanical propagator. Then, we briefly review the theory of diffusion-influenced reactions and discuss the PDX for the classical theory and the Doi (also referred to as volume reactivity) model. We explicitly show that we can recover the GF of an isolated pair from the PDX for the case of the SCK theory (implemented as $\delta$-function potential) in one dimension (1D) and for the volume reactivity model in 2D.

2 Theory

2.1 The Path Decomposition Expansion

The PDX was developed in Refs. [4] to study quantum tunneling, subsequently it has been used for other applications as well, see Refs. [13, 22]. In Refs. [28, 29], this technique was used to calculate the Feynmann propagator for a $\delta$- and step-function potential in an elegant and simple way. We point out that these potentials correspond exactly to the SCK and Doi model in the context of theories of diffusion-influenced reactions, as we will expand on later. Here, we consider a quantum mechanical particle in 1D. Then, the propagator satisfies the following convolution relation [4, 22, 28, 29]:

$$K(x, t|x_0) = \frac{i\hbar}{2m} \int_0^t K(x, t|a, \tau) \frac{\partial K^\tau(\xi, \tau|x_0, 0)}{\partial \xi} \bigg|_{\xi=a} d\tau. \quad (7)$$

This relation means that every path can be split into a restricted part (represented by $K^\tau$) that starts at $x_0$ at time $t_0 = 0$, never crosses the boundary at $x = a = 0$, but that ends at the boundary at time $\tau$, and an unrestricted
part (represented by $K$) that starts at the boundary at time $\tau$ and ends at $x$ at time $t$. Similarly, one has

$$K(x,t|x_0) = -\frac{i\hbar}{2m} \int_0^t \frac{\partial K^r(x,t|\xi,\tau)}{\partial \xi} \bigg|_{\xi=a} K(a,\tau|x_0,0)d\tau,$$  

which corresponds to a split into an unrestricted part that starts at $x_0$ at time $t_0 = 0$, may cross the boundary $x = a = 0$ many times, and finally ends at the boundary after time $\tau$ and a restricted part that starts at the boundary at time $\tau$, never crosses the boundary after that and ends at $x$ at time $t$. Combining these two formulas (Eqs. (7), (8)), one obtains for the Feynmann propagator

$$K(x,t|x_0) = \frac{\hbar^2}{4m^2} \int_0^t dT \int_0^T d\tau \frac{\partial K^r(x,t|\xi,T)}{\partial \xi} \bigg|_{\xi=a} \times K(a,T|a,\tau) \frac{\partial K^r(\xi,\tau|x_0,0)}{\partial \xi} \bigg|_{\xi=a}.$$  

(9)

Refs. [28, 29] exploit that the three quantities on the rhs of Eq. (9) can be easier calculated than the full propagator $K(x,t|x_0)$. This convolution relation (Eq. (9)) is the central identity that we will use in the following and we will explicitly check that it holds true in theories of diffusion-influenced reactions as well.

2.2 Smoluchowski-Collins-Kimball theory

The theory of diffusion-influenced reactions is traditionally described by the diffusion equation (Eq. (3)) with vanishing $V(x)$, subject to a suitable BC that implements the physics at the encounter distance. The Collins-Kimball BC [7], also referred to as radiation BC, generalizes the Smoluchowski (or absorbing) BC [25] and reads

$$D \frac{\partial p_{\text{rad}}(x,t|x_0)}{\partial x} \bigg|_{x=a} = \kappa_a p_{\text{rad}}(x=a,t|x_0).$$  

(10)

In the limits $\kappa_a \to \infty$ and $\kappa_a \to 0$, the radiation BC reduces to the absorbing and non-reactive (reflective) BC, respectively. The survival probability is defined as

$$S_{\text{rad}}(t) = \int_a^\infty p_{\text{rad}}(x,t|x_0)dx.$$  

(11)
Now we may invoke the diffusion equation (Eq. (3), \( V(x) = 0 \)) and the
definition of the survival probability (Eq. (11)), which tells us that
\[
- \frac{\partial S_{\text{rad}}(t|x_0)}{\partial t} = D_{\text{rad}} \frac{\partial p_{\text{rad}}(x,t|x_0)}{\partial x} \bigg|_{x=a}.
\]
(12)

Note that this relation is true independent of the imposed BC at the en-
counter distance. However, if we impose an absorbing BC, the negative time
derivative of the survival probability bears a special meaning. It is the first
passage time PDF
\[
f_{FP}(t|x_0) := -\frac{\partial S_{\text{abs}}(t|x_0)}{\partial t}.
\]
(13)
Furthermore, in the case of a radiation BC, the quantity \( \kappa_a p_{\text{rad}}(a,t|a) \) is the
rebinding time PDF that plays an essential role in understanding spatial
stochastic fluctuations [24, 16]. Owing to the Collins-Kimball BC (Eq. (10)
and Eq. (12) one has
\[
f_{\text{reb}}(t) := -\frac{\partial S_{\text{rad}}(t|x_0 = a)}{\partial t} = \kappa_a p_{\text{rad}}(a,t|a).
\]
(14)
Finally, it will turn out to be convenient to consider the PDF \( f_{LR}(\tau|x,t) \) for
the last reflection time \( \tau \) before \( t \), given that the molecule is located at \( x \) at
time \( t \), which is closely related to the first passage time PDF via
\[
f_{LR}(\tau|x,t) = f_{FP}(t - \tau|x).
\]
(15)

As already mentioned, an alternative and more general approach, that
abandons the requirement of a BC at the encounter distance, implements
the chemical reaction by adding appropriate sink terms to the equation of
motion, i.e. one deals with a diffusion equation featuring a non-vanishing
potential (Eq. (3)). For instance, the SCK model may be defined by the
diffusion equation with \( V(x) = -\kappa_a \delta(x - a) \), while for volume reaction
theories the potential assumes the form \( V(x) = -\kappa_a \Theta(a - x) \).

In the following, we will focus on these two examples and show that the
corresponding full propagator can be obtained by a convolution relation that
is analog to Eq. (9). More precisely, one has
\[
p_V(x,t|x_0) = \pm D^2 \int_0^T d\tau \int_0^T dT \frac{\partial p_{\text{abs}}(x,t - T|\xi)}{\partial \xi} \bigg|_{\xi=a}
\]
\[
p_V(a,T - \tau|a) \frac{\partial p_{\text{abs}}(\xi,\tau|x_0)}{\partial \xi} \bigg|_{\xi=a}.
\]
(16)
Note that if both \(x, x_0 > a\) or \(x, x_0 < a\), one has to add a second term \(-p_{\text{abs}}(x,t|x_0)\) on the lhs of Eq. (13). These two cases also correspond to the positive sign on the rhs, while the cases \(x < a, x_0 > a\) and \(x > a, x_0 < a\) correspond to the negative sign. Furthermore, Eq. (13) shows that the restricted propagator \(K^r\) in the quantum mechanical version (Eq. (9)) corresponds to the GF \(p_{\text{abs}}\) with absorbing BC. However, we emphasize that \(p_{\text{abs}}\) may describe propagation in the presence of an absorbing boundary and a non-vanishing potential.

### 2.3 Partially absorbing trap in one dimension

To check the validity of Eq. (16), we consider a partially absorbing trap in one dimension at \(x = a = 0\). Instead of following the classical route via imposing a radiation BC, one may employ the following equation of motion [8, 23]

\[
\frac{\partial p_\delta(x,t|x_0)}{\partial t} = \left[D \frac{\partial^2}{\partial x^2} - \kappa_\delta(x)\right] p_\delta(x,t|x_0).
\]  

(17)

The GF solution \(p_\delta(x,t|x_0)\) has been presented in Ref. [8]. Note that this GF is not given by exactly the same expression as the solution \(p_{\text{rad}}(x,t|x_0)\) of the corresponding radiation BC problem, as detailed in Ref. [23]. In particular, the GF \(p_\delta(x,t|x_0)\) is defined for all \(-\infty < x, x_0 < \infty\), in contrast to the SCK solution \(p_{\text{rad}}(x,t|x_0)\) that is restricted to the semi-infinite line, \(0 < x, x_0 < \infty\). In the following, we will focus on the case \(x < 0, x_0 > 0\), but all other cases can be treated similarly.

We observe that in the \(\delta\)-function case, the convolution relation (Eq. (16)) may be rewritten in the Laplace domain as product of three prominent waiting time PDF. To see this, we first note that in the present context one has to take into account two different first passage time PDF, corresponding to \(x_0 < 0\) and \(x_0 > 0\). More precisely,

\[
f_{FP}^<(t|x_0) = \frac{\partial S_{\text{abs}}^<(t|x_0)}{\partial t}, \quad S_{\text{abs}}^<(t|x_0) := \int_{-\infty}^{0} p_{\text{abs}}^<(x,t|x_0)dx, \quad x < 0,
\]

(18)

\[
f_{FP}^>(t|x_0) = \frac{\partial S_{\text{abs}}^>(t|x_0)}{\partial t}, \quad S_{\text{abs}}^>(t|x_0) := \int_{0}^{\infty} p_{\text{abs}}^>(x,t|x_0)dx, \quad x > 0.
\]

(19)

Furthermore, one has (see Eqs. (12), (13), (15))

\[
f_{LR}^< (T|x,t) = f_{FP}^<(t - T|x) = -D\frac{\partial p_{\text{abs}}^<(x,t-T|\xi)}{\partial \xi} \bigg|_{\xi = a}, \quad x < 0,
\]

(20)

\[
f_{FP}^>(t|x_0) = D\frac{\partial p_{\text{abs}}^>(\xi,t|x_0)}{\partial \xi} \bigg|_{\xi = a}, \quad x > 0.
\]

(21)
Next, we would also like to point out that, although \( p_{\text{rad}}(x, t|x_0) \) is different from \( p_{\delta}(x, t|x_0) \) for general \( x, x_0 \), one has

\[
p_{\text{rad}}(0, t|0) = 2p_{\delta}(0, t|0),
\]

and

\[
S_{\delta}(t|x_0) = S_{\text{rad}}(t|x_0), \quad x_0 > 0,
\]

where

\[
S_{\delta}(t|x_0) := S_{\delta}^\geq(t|x_0) + S_{\delta}^\leq(t|x_0) := \int_0^\infty p_{\delta}(x, t|x_0)dx + \int_{-\infty}^0 p_{\delta}(x, t|x_0)dx
\]

as discussed in Ref. [23]. Thus, using Eqs. (16), (14), (15), (20), (21) and (22), we can substitute the first passage and rebinding time PDF for the spatial derivative terms and for \( \tilde{p}_{\delta}(a, s|a) \), respectively, in Eq. (16) to obtain

\[
\tilde{p}_{\delta}(x, s|x_0) = 1/2 \kappa \tilde{f}_{LR}^\leq(s|x) \tilde{f}_{\text{reb}}(s) \tilde{f}_{FP}^\geq(s|x_0), \quad x < 0, \ x_0 > 0,
\]

where we employed the following notation for the Laplace transform of a function \( g(t) \)

\[
\mathcal{L}[g](s) := \tilde{g}(s) := \int_0^\infty e^{-st}g(t)dt.
\]

One may also verify Eq. (25) explicitly. Transforming the solution given in Ref. [8] to the Laplace domain, one arrives at

\[
\tilde{p}_{\delta}(x, s|x_0) = \frac{1}{2\kappa} \tilde{f}_{LR}^\leq(s|x) \tilde{f}_{\text{reb}}(s) \tilde{f}_{FP}^\geq(s|x_0), \quad x < 0, \ x_0 > 0,
\]

where \( v := \sqrt{s/D} \) and \( h := \kappa a/D \). Then, using the expressions for the GF with absorbing BC in the Laplace domain [5]

\[
\tilde{p}_{\text{abs}}^\leq(x, s|x_0) = \frac{1}{2Dv} \left[ e^{-v|x-x_0|} - e^{-v|x+x_0|} \right], \quad x, x_0 < 0,
\]

\[
\tilde{p}_{\text{abs}}^\geq(x, s|x_0) = \frac{1}{2Dv} \left[ e^{-v|x-x_0|} - e^{-v(x+x_0)} \right], \quad x, x_0 > 0,
\]

we obtain

\[
\tilde{f}_{FP}^\leq(s|x_0) = e^{-\sqrt{s/\kappa v D}}, \quad (30)
\]

\[
\tilde{f}_{FP}^\geq(s|x_0) = e^{-\sqrt{s/\kappa v D}}. \quad (31)
\]

Using Eqs. (27), (30) and (31), we see that Eq. (25) does indeed hold true.
2.4 Area reactivity model

The second example that we discuss is the area reactivity model in 2D [14 18 19], also referred to as Doi model in the case of an irreversible reaction [9 10 2]. The equation of motion reads

$$\frac{\partial p_{\Theta}(r, t|r_0)}{\partial t} = \left[ D \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) - \kappa_r \Theta(a-r) \right] p_{\Theta}(r, t|r_0).$$

(32)

In the following, we will show that

$$\tilde{p}_{\Theta}(r, s|r_0) = \pm \frac{4\pi^2 a^2 D^2}{2\pi aD} \frac{\partial \tilde{p}_{abs}(r, s|\xi)}{\partial \xi} \bigg|_{\xi=a}$$

(33)

Again, if both \(r, r_0 > a\) or \(r, r_0 < a\), one has to add a second term \(-\tilde{p}_{abs}(r, s|r_0)\) on the lhs of Eq. (33), as in the 1D case discussed before.

Furthermore, we emphasize that, although we consider here explicitly the irreversible reaction, Eq. (33) remains valid for the reversible case. In fact, one only has to substitute \(w := \sqrt{(s + \kappa_r)/s} \rightarrow \sqrt{(s + \kappa_r + \kappa_d)/(s + \kappa_d)}\), see Ref. [19].

To be definite, we consider the case \(r_0 > a, r < a\). Then, one has [18 19]

$$\tilde{p}_{\Theta}(r, s|r_0) = I_0(wr)K_0(vr_0),$$

(34)

where \(I_{0,1}, K_{0,1}\) refer to the modified Bessel function of first and second kind, respectively, and zeroth and first order, see Ref. [11 Sec. 9.6].

Let us now turn to the GF \(p_{abs}(r, t|r_0)\) satisfying absorbing BC. Similarly to the 1-D \(\delta\)-function case considered before, one has to take into account two different GF \(p_{abs}\), corresponding to the domains \(r, r_0 > a\) and \(r, r_0 < a\). For \(r > a, r_0 > a\), one has in the Laplace domain

$$\tilde{p}_{abs}(r, s|r_0) = \tilde{p}_{free}(r, v|r_0) - \frac{1}{2\pi D} K_0(vr) K_0(vr_0) \frac{I_0(va)}{K_0(va)},$$

(36)

where

$$\tilde{p}_{free}(r, s|r_0) = \frac{1}{2\pi D} \left\{ \begin{array}{ll} I_0(vr_0)K_0(vr), & r > r_0 \\ I_0(vr)K_0(vr_0), & r < r_0 \end{array} \right.$$ 

(37)

It follows that

$$\left. 2\pi aD \frac{\partial \tilde{p}_{abs}(\xi, s|r_0)}{\partial \xi} \right|_{\xi=a} = \frac{K_0(vr_0)}{K_0(va)}.$$ 

(38)
Next, for \( r < a, r_0 < a \), one has

\[
\tilde{p}_{\text{abs}}^<(r, s|r_0) = \tilde{p}_{\text{free}}(r, w|r_0) - \frac{1}{2\pi D} I_0(wr) I_0(wr_0) \frac{K_0(wa)}{I_0(wa)}. \tag{39}
\]

Note that the appearance of \( w \) instead of \( v \) is due to the fact that within the domain \( r < a \) the molecule moves in the presence of a constant potential given by \( -\kappa_r \). Thus, one obtains

\[
2\pi a D \left. \frac{\partial \tilde{p}_{\text{abs}}^<(r, s|\xi)}{\partial \xi} \right|_{\xi=a} = \frac{I_0(wr)}{I_0(wa)}. \tag{40}
\]

Finally, using Eqs. \( \text{(34)}, \text{(38)} \) and \( \text{(40)} \), we can verify that indeed Eq. \( \text{(33)} \) does hold true. Similarly, one can show that Eq. \( \text{(33)} \) is fulfilled by the GF corresponding to \( r, r_0 > a \) and \( r, r_0 < a \), as well as by the GF describing the reversible reaction.

Finally, note that if we used for \( r < a \) the expression \(-\partial S_{\text{abs}}^<(t|r)/\partial t\), instead of the flux (Eq. \( \text{(40)} \)) we would not recover the full propagator. The reason is that in the case of a \( \delta \)-function potential the flux is equal to the negative time derivative of the survival probability (up to a sign, cf. Eqs. \( \text{(20)}, \text{(21)} \)). However, in the AR model, due to the \( \Theta \)-potential, one has instead

\[
\frac{\partial S_{\text{abs}}^<(t|r_0)}{\partial t} = 2\pi a D \left. \frac{\partial \tilde{p}_{\text{abs}}^<(r, t|r_0)}{\partial r} \right|_{r=a} - \kappa_r S_{\text{abs}}^<(t|r_0). \tag{41}
\]

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