Exact transient solutions of kinetics of first-order reactions with end effects

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The finite set of rate equations

$$C'_{m,n}(t) = \alpha_{n,n-1}C_{m,n-1}(t) + \alpha_{n,n}C_{m,n}(t) + \alpha_{n,n+1}C_{m,n+1}(t),$$
$$0 \leqslant m \leqslant N,\ 0 \leqslant n \leqslant N,$$

where $\alpha_{i,j}$ are $\alpha_{j,j-1} = A$, $\alpha_{j,j} = -(A+B)$, $\alpha_{j,j+1} = B$, with $\alpha_{0,0} = -\alpha_{1,0} = -a$ and $\alpha_{N,N} = -\alpha_{N-1,N} = -b$, $\alpha_{0,-1} = \alpha_{N,N+1} = 0$, subject to the initial condition $C_{m,n}(0) = \delta_{n,m}$ (Kronecker delta) for some m, arises in a number of applications of mathematics and mathematical physics. We show that there are five sets of values of a and b for which the above system admits exact transient solutions.

1. Introduction

The interest in the fluctuations and in the stochastic methods describing them has grown enormously. One-step (or generation–recombination or birth–death) processes are a special class of Markov processes, having applications in diverse physical problems such as gas phase relaxation processes, chemical kinetics, spin relaxation processes and polymer dynamics [3,5,7,13,17,19]. In particular, the system of equations

$$\begin{aligned}
C'_{m,0}(t) &= -aC_{m,0}(t) + BC_{m,1}(t),\\
C'_{m,1}(t) &= aC_{m,0}(t) - (A+B)C_{m,1}(t) + BC_{m,2}(t),\\
C'_{m,n}(t) &= AC_{m,n-1}(t) - (A+B)C_{m,n}(t) + BC_{m,n+1}(t),\\
&\qquad 2 \leqslant n \leqslant N-2,\\
C'_{m,N-1}(t) &= AC_{m,N-2}(t) - (A+B)C_{m,N-1}(t) + bC_{m,N}(t),\\
C'_{m,N}(t) &= AC_{m,N-1}(t) - bC_{m,N}(t),
\end{aligned} \tag{1.1}$$

subject to the initial condition $C_{m,n}(0) = \delta_{n,m}$ (Kronecker delta) for some m, arises in a number of applications of mathematics and mathematical physics [1,15,16]. Special cases of these equations have already received considerable attention [4,21]. Ninham et al. [12] have discussed this system to describe the kinetics of the helix–coil transition in polypeptides, when it is assumed that helical regions nucleate at one end of the coil and thereafter grow towards the other end of the molecule. Then $C_{m,n}(t)$ represent the concentration of molecules containing n "helix" and $N-n$ "coil" units at time t, given that there were m helix units initially. Here N denotes the chain length. At any time, the rate at which the number of helix units increase from n to $n+1$ is described by A, and the rate at which the number of helix units decrease from n to $n-1$ is described by B. Also, the rates at which the number of helix units increase from 0 to 1 and decrease from N to $N-1$ are described by a and b, respectively.

In this paper we obtain exact time-dependent solutions of system (1.1) with $a \neq A$ and $b \neq B$. Transient analysis helps us to understand the behaviour of a system better when the parameters are perturbed. For all values of a and b it is possible to find transient solutions of this system numerically. In order to achieve the exact transient solution of this system analytically, we consider the cases where

$$a \in \{A, A+\sqrt{AB}, A-\sqrt{AB}\}, \qquad b \in \{B, B+\sqrt{AB}, B-\sqrt{AB}\}.$$

To ensure the positivity of the parameters we discard the case $a = A-\sqrt{AB},\ b = B-\sqrt{AB}$. These transient solutions are the same when $a,\ A$ and $C_{m,n}(t)$ are replaced by $b,\ B$ and $C_{m,N-n}(t)$, respectively. Because of this symmetric nature, the remaining eight cases reduce to five cases. In section 3, the exact transient solutions are obtained for these five cases and the equilibrium solutions are deduced.

In addition to the helix–coil transition problem such as the effect of defects, the explicit solution to equations (1.1) may also be of value as it provides a model calculation in the theory of multi-state relaxation processes; errors introduced by the replacement of equations (1.1) by the continuum analog (viz. the Fokker–Planck equation) can be bounded precisely. The model can also be used to test the utility of the concept of "mean relaxation time". When $a = A$ and $b = B$, this system of equations appears in the theory of queues [22]. If $A = B$ and periodic boundary conditions are imposed, the equations describe a one-dimensional symmetric continuous-time random walk on a circle. In the latter form, the equations have been studied in connection with the relaxation of a one-dimensional Ising model and in describing the denaturation of DNA. When $A = B$ and the rate constants a and b in the equations for $C'_{m,1}(t)$ and $C'_{m,N-1}(t)$ are replaced by A, the eigenvalues of the system are identical with those of a one-dimensional system of coupled harmonic oscillators with either free or fixed ends [12]. Equations (1.1) are used to obtain the velocity and the diffusion constant for a periodic one-dimensional hopping model [2].

2. Some useful identities

In this section, some identities and polynomials used to prove the main results are given.

Identity 1.

$$\begin{vmatrix} 2\cos\theta & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & 2\cos\theta & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & 2\cos\theta & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & 2\cos\theta \end{vmatrix}_{n\times n} = \frac{\sin(n+1)\theta}{\sin\theta}, \quad n \geqslant 1. \tag{2.1}$$

Identity 2.

$$\prod_{k=1}^{N}\left(\cos y - \cos\frac{k\pi}{N+1}\right) = 2^{-N}\frac{\sin(N+1)y}{\sin y}. \tag{2.2}$$

We obtain the above identity by making use of the following trigonometric identities ((91.2.9) and (91.2.13) from [6]):

$$\prod_{k=1}^{[(n-1)/2]}\left(\cos y - \cos\frac{2k\pi}{n}\right) = \begin{cases} 2^{(1/2)-n/2}\sin\left(\frac{ny}{2}\right)\csc\left(\frac{y}{2}\right) & (n \text{ odd}), \\ 2^{1-(n/2)}\sin\left(\frac{ny}{2}\right)\csc y & (n \text{ even}), \end{cases}$$

$$\prod_{k=0}^{[(n-1)/2]}\left\{\cos y - \cos\left[(2k+1)\frac{\pi}{n}\right]\right\} = \begin{cases} 2^{(1/2)-n/2}\cos\left(\frac{ny}{2}\right)\sec\left(\frac{y}{2}\right) & (n \text{ odd}), \\ 2^{1-(n/2)}\cos\left(\frac{ny}{2}\right) & (n \text{ even}). \end{cases}$$

Identity 3.

$$\prod_{\substack{k=1 \\ k\neq r}}^{N}\left(\cos\frac{r\pi}{N} - \cos\frac{k\pi}{N}\right) = \frac{N(-1)^{r+1}}{2^{(N-1)}} \times \begin{cases} \frac{1+\cos(r\pi/N)}{\sin^2(r\pi/N)}, & r < N, \\ 1, & r = N. \end{cases} \tag{2.3}$$

The transient solution of (1.1) will be expressed in terms of two sequences of polynomials. Define the polynomials $Q_r(s)$ $(r = 1, 2, \ldots, N)$ recursively as

$$\begin{aligned} Q_0(s) &= 1, \\ Q_1(s) &= s + b, \\ Q_2(s) &= (s + A + B)Q_1(s) - Ab, \\ Q_r(s) &= (s + A + B)Q_{r-1}(s) - ABQ_{r-2}(s), \quad 3 \leqslant r \leqslant N, \end{aligned} \tag{2.4}$$

$$Q_{N+1}(s) = (s + a)Q_N(s) - aBQ_{N-1}(s). \tag{2.5}$$

The above can be expressed in terms of the polynomials $P_r(s)$ $(r = 1, 2, \ldots, N)$ and are defined recursively as

$$\begin{aligned} P_0(s) &= 1, \\ P_1(s) &= s + a, \\ P_2(s) &= (s + A + B)P_1(s) - aB, \end{aligned}$$

$$P_r(s) = (s + A + B)P_{r-1}(s) - ABP_{r-2}(s), \quad 3 \leqslant r \leqslant N, \tag{2.6}$$

$$P_{N+1}(s) = (s + b)P_N(s) - AbP_{N-1}(s). \tag{2.7}$$

Here $P_r(s)$ and $Q_r(s)$ are of degree r with coefficient 1 for s^r. Further, we use the following notation:

$$D_{m,n} = \begin{cases} aA^{n-1}, & m = 0,\ n > 0, \\ bB^{N-n-1}, & m = N,\ n < N, \\ 1, & m = n, \end{cases}$$

and, for $1 \leqslant m \leqslant N - 1$,

$$D_{m,n} = \begin{cases} B^{m-n}, & n < m, \\ A^{n-m}, & n > m. \end{cases} \tag{2.8}$$

Now we obtain the exact transient solution of the concentration of molecules at time t.

3. Transient solution

In this section, we obtain the transient solution of system (1.1) analytically with $a \neq A,\ b \neq B$. This is in contrast to the computational difficulties encountered when the diagonal elements of the underlying matrix become large, for some values of the parameters, causing overflow while running the program. When $a = A$ and $b = B$, there exist a number of methods to find the time dependent solution of (1.1) like the fundamental matrix approach of Takács [22], transformation approach of Morse [11], Laplace transform method of Srivatsava and Kashyap [20] and continued fraction approach of Parthasarathy and Lenin [16]. These techniques involve matrix exponentials which are extensively studied [8–10]. However, we adopt suitably the method of Rosenlund [18], which is more pertinent to the problem at hand.

Theorem 1. The exact transient solution of the concentration of molecules at time t is given for $0 \leqslant m \leqslant N$ by

$$C_{m,n}(t) = C_n + \sum_{r=1}^{N} \frac{D_{m,N}D_{N,n}P_n(-\beta_r)P_m(-\beta_r)\exp(-\beta_r t)}{P_N(-\beta_r)P'_{N+1}(-\beta_r)}, \quad n = 0, 1, \ldots, N, \tag{3.1}$$

where

$$C_n = \frac{D_{m,N}D_{N,n}P_n(0)P_m(0)}{P_N(0)\left(\prod_{r=1}^{N}\beta_r\right)}, \tag{3.2}$$

$$P'_{N+1}(-\beta_r) = -\beta_r \prod_{\substack{k=1 \\ k\neq r}}^{N} (\beta_k - \beta_r), \quad r = 1, 2, \ldots, N. \tag{3.3}$$

$D_{m,n}$ are defined as in (2.8) and β_r are the zeros of $P_{N+1}(s)$.

Proof. Letting, for $s > 0$,

$$\widehat{C}_{m,n}(s) = \int_0^\infty \mathrm{e}^{-st} C_{m,n}(t)\,\mathrm{d}t, \tag{3.4}$$

Laplace transformation of (1.1) gives

$$\begin{aligned}
s\widehat{C}_{m,0}(s) - \delta_{0,m} &= -a\widehat{C}_{m,0}(s) + B\widehat{C}_{m,1}(s),\\
s\widehat{C}_{m,1}(s) - \delta_{1,m} &= a\widehat{C}_{m,0}(s) - (A+B)\widehat{C}_{m,1}(s) + B\widehat{C}_{m,2}(s),\\
s\widehat{C}_{m,n}(s) - \delta_{n,m} &= A\widehat{C}_{m,n-1}(s) - (A+B)\widehat{C}_{m,n}(s) + B\widehat{C}_{m,n+1}(s),\\
&\qquad\qquad 2 \leqslant n \leqslant N-2,\\
s\widehat{C}_{m,N-1}(s) - \delta_{N-1,m} &= A\widehat{C}_{m,N-2}(s) - (A+B)\widehat{C}_{m,N-1}(s) + b\widehat{C}_{m,N-1}(s),\\
s\widehat{C}_{m,N}(s) - \delta_{N,m} &= A\widehat{C}_{m,N-1}(s) - b\widehat{C}_{m,N}(s).
\end{aligned} \tag{3.5}$$

For each m this defines a linear system with $N+1$ equations. Define its $N+1$ by $N+1$ matrix $E(s)$ $(= (a_{m,n}))$ as

$$E(s) = \begin{pmatrix}
s+a & -B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
-a & s+A+B & -B & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & -A & s+A+B & -B & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & -A & s+A+B & -b\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -A & s+b
\end{pmatrix}.$$

Then we can write (3.5) in the matrix form:

$$E(s)\bigl[\widehat{C}_{m,0}(s), \widehat{C}_{m,1}(s), \ldots, \widehat{C}_{m,N}(s)\bigr]^{\mathrm{T}} = [\delta_{0,m}, \delta_{1,m}, \ldots, \delta_{N,m}]^{\mathrm{T}}. \tag{3.6}$$

From (2.7) and (2.5), we observe that $P_{N+1}(s) = Q_{N+1}(s) = |E(s)|$, i.e.,

$$P_{N+1}(s) = \begin{vmatrix}
s+a & -B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
-a & s+A+B & -B & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & -A & s+A+B & -b\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -A & s+b
\end{vmatrix}$$

$$= s\begin{vmatrix}
s+a+B & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
A & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot\\
\cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & B\\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+b
\end{vmatrix}_N.$$

It is well known that $P_{N+1}(s)$ has $N+1$ distinct, real zeros

$$\beta_0 < \beta_1 < \cdots < \beta_N \tag{3.7}$$

and $\beta_0 = 0$; then we can write

$$P_{N+1}(s) = s\prod_{r=1}^{N}(s+\beta_r). \tag{3.8}$$

By (3.7), $|E(s)| > 0$ and (3.6) has a unique solution for $s > 0$. The solution of (3.6) by Cramer's rule is written as

$$\widehat{C}_{m,n}(s) = \frac{\widehat{B}_{m,n}(s)}{|E(s)|}, \tag{3.9}$$

where $\widehat{B}_{m,n}(s)$ is obtained from $|E(s)|$ by replacing the nth column with $[\delta_{0,m}, \delta_{1,m}, \ldots, \delta_{N,m}]^{\mathrm{T}}$. Thus $\widehat{B}_{m,n}(s)$ is the cofactor of the element $a_{m,n}$, and this is easily found to be

$$\widehat{B}_{m,n}(s) = D_{m,n} \times \begin{cases} P_n(s)Q_{N-m}(s), & n < m, \\ P_m(s)Q_{N-n}(s), & n > m, \\ P_n(s)Q_{N-n}(s), & n = m, \end{cases}$$

where $D_{m,n}$, $P_n(s)$ and $Q_n(s)$ are defined as in (2.8), (2.6) and (2.4), respectively. Substituting the above in (3.9), we get

$$\widehat{C}_{m,n}(s) = \frac{D_{m,n}Q_{N-\max(m,n)}(s)P_{\min(m,n)}(s)}{P_{N+1}(s)}, \quad 0 \leqslant m \leqslant N,\ 0 \leqslant n \leqslant N.$$

Using (3.8), the inversion of the above gives

$$C_{m,n}(t) = C_n + \sum_{r=1}^{N} b_{m,n,r}\exp(-\beta_r t), \tag{3.10}$$

where

$$b_{m,n,r} = \frac{D_{m,n}Q_{N-\max(m,n)}(-\beta_r)P_{\min(m,n)}(-\beta_r)}{P'_{N+1}(-\beta_r)} \tag{3.11}$$

and C_n is defined as in (3.2). Note that the term corresponding to $r = 0$ and $\beta_0 = 0$ is the limit of $C_{m,n}(t)$ as $t \to \infty$ and, hence, equal to C_n. Also note that, at the zeros of $P_{N+1}(s)$,

$$Q_{N-n}(-\beta_r) = \frac{D_{m,N}D_{N,n}P_m(-\beta_r)}{D_{m,n}P_N(-\beta_r)}.$$

Substituting the above in (3.11), we obtain

$$b_{m,n,r} = \frac{D_{m,N}D_{N,n}P_n(-\beta_r)P_m(-\beta_r)}{P_N(-\beta_r)P'_{N+1}(-\beta_r)}. \tag{3.12}$$

Theorem follows by substituting the above in (3.10). □

In view of the representation formula (3.1), the problem of finding the transient solution for the system given its rate parameters amounts to finding the orthogonal polynomials $P_n(s)$ $(n = 1, \ldots, N)$ and the zeros of $P_{N+1}(s)$ from the parameters in the recurrence relations. Often it will be difficult to find the transient solution for such systems explicitly. In the next theorem, we find the explicit expression for $P_n(s)$.

Explicit expression of $P_n(s)$

Theorem 2. For $n = 1, 2, \ldots, N$,

$$P_n(s) = \frac{(AB)^{n/2}}{\sin\theta}\left\{ \sin(n+1)\theta - \left(\frac{A+B-a}{\sqrt{AB}}\right)\sin n\theta + \left(\frac{A-a}{A}\right)\sin(n-1)\theta \right\}, \tag{3.13}$$

where $s + A + B = 2\sqrt{AB}\cos\theta$.

Proof. From (2.6), we find for $n = 1, 2, \ldots, N$,

$$\begin{aligned} P_n(s) &= \begin{vmatrix} s+a & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ a & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & B \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B \end{vmatrix}_n \\ &= \begin{vmatrix} s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ A & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & B \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B \end{vmatrix}_n \\ &\quad + \begin{vmatrix} a-A-B & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ a-A & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & B \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B \end{vmatrix}_n . \end{aligned} \tag{3.14}$$

By dividing $\sqrt{AB}$ in each row or each column, putting $s + A + B = 2\sqrt{AB}\cos\theta$ and using relation (2.1), we obtain

$$P_n(s) = \frac{1}{\sin\theta}\left[\left(\sqrt{AB}\,\right)^n \sin(n+1)\theta - (A+B-a)\left(\sqrt{AB}\,\right)^{n-1}\sin n\theta + B(A-a)\left(\sqrt{AB}\,\right)^{n-2}\sin(n-1)\theta\right].$$

Therefore (3.13) follows. $\square$

Exact zeros of $P_{N+1}(s)$

Solution (3.1) is completely known if we have the exact zeros of $P_{N+1}(s)$. We show that there are five sets of values for a and b for which exact solutions are possible to obtain. Now we obtain the exact zeros of $P_{N+1}(s)$ for the five cases.

Writing (2.7) in the matrix form, we obtain

$$P_{N+1}(s) = \begin{vmatrix} s+a & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ a & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & A & s+A+B & B & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & b \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+b \end{vmatrix}_{N+1}$$

$$= s \begin{vmatrix} s+a+B & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ A & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & A & s+A+B & B & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & B \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+b \end{vmatrix}_{N}.$$

By dividing $\sqrt{AB}$ in each row or each column, putting $s+A+B = 2\sqrt{AB}\cos\theta$ and using identity (2.1), we get

$$P_{N+1}(s) = s\frac{(AB)^{N/2}}{\sin\theta}\left\{ \sin(N+1)\theta + \left(\frac{a+b-(A+B)}{\sqrt{AB}}\right)\sin N\theta + \frac{(a-A)(b-B)}{AB}\sin(N-1)\theta \right\}. \tag{3.15}$$

From the right-hand side of the above equation, we observe that zero is a root of $P_{N+1}(s)$ so that $\beta_0 = 0$. Remaining N zeros can be obtained from the following equation:

$$\sin(N+1)\theta + \left(\frac{a+b-(A+B)}{\sqrt{AB}}\right)\sin N\theta + \frac{(a-A)(b-B)}{AB}\sin(N-1)\theta = 0.$$

We are interested to obtain the roots of the above equation (in turn, the values of θ) in closed form. We observe that, if

$$a \in \{A, A+\sqrt{AB}, A-\sqrt{AB}\}, \qquad b \in \{B, B+\sqrt{AB}, B-\sqrt{AB}\},$$

using the trigonometric relation

$$\sin(A-B)\theta + \sin(A+B)\theta = 2\sin A\theta\cos B\theta \tag{3.16}$$

we can obtain the roots in closed form. This leads to nine possible cases of a and b for which exact zeros β_r $(r = 1, 2, \ldots, N)$ are possible to obtain, but to ensure the

Table 1
Five cases of a and b and the corresponding zeros of $P_{N+1}(s)$.

Case	a	b	β_r $(0 \leqslant r \leqslant N)$
I	A	B	$0,\ A+B-2\sqrt{AB}\cos\left(\frac{r}{N+1}\pi\right),\ A,B>0$
II	$A+\sqrt{AB}$	B	$0,\ A+B-2\sqrt{AB}\cos\left(\frac{2r}{2N+1}\pi\right),\ A,B>0$
III	$A+\sqrt{AB}$	$B+\sqrt{AB}$	$0,\ A+B-2\sqrt{AB}\cos\left(\frac{r}{N}\pi\right),\ A,B>0$
IV	$A-\sqrt{AB}$	B	$0,\ A+B-2\sqrt{AB}\cos\left(\frac{2r-1}{2N+1}\pi\right),\ A>B>0$
V	$A-\sqrt{AB}$	$B+\sqrt{AB}$	$0,\ A+B-2\sqrt{AB}\cos\left(\frac{2r+1}{2N+1}\pi\right),\ A>B>0$

positivity of the rates we discard the case $a = A-\sqrt{AB},\ b = B-\sqrt{AB}$. We observe that equation (3.15) is symmetric with respect to a and b. Also, system (1.1) is the same when $a,\ A$ and $C_{m,n}(t)$ are replaced by $b,\ B$ and $C_{m,N-n}(t)$, respectively. Because of this symmetric nature, the eight cases reduce to five cases. The zeros of $P_{N+1}(s)$ and the conditions on A and B to ensure the positiveness are tabulated in table 1.

Equilibrium solutions

Since one of the zeros of $P_{N+1}(s)$ is zero (i.e., $\beta_0 = 0$), equilibrium solutions C_n $(n = 0, 1, \ldots, N)$ exist and are obtained by letting $t \to \infty$ in (1.1):

$$\begin{aligned} C_0 &= BbF, \\ C_n &= ab\gamma^{n-1}F, \quad n = 1, 2, \ldots, N-1, \\ C_N &= aB\gamma^{N-1}F, \end{aligned} \tag{3.17}$$

where

$$\gamma = \frac{A}{B},$$
$$F = \frac{(1-\gamma)}{B^2(1-\gamma^{N+1}) + B(A+B-a-b)(1-\gamma^N) + (A-a)(B-b)(1-\gamma^{N-1})}.$$

Now, we shall see the exact results for the five cases in the following theorems.

Explicit solutions of $C_{m,n}(t)$

Theorem 3. The exact transient solution for case I (i.e., $a = A, b = B$) is given by

$$\begin{aligned} C_{m,n}(t) = {} & \frac{(1-\gamma)\gamma^n}{(1-\gamma^{N+1})} + \frac{2\gamma^{1+(n-m)/2}}{N+1} \sum_{r=1}^{N} \frac{\mathrm{e}^{-(A+B)t+2\sqrt{AB}t\cos(r\pi/(N+1))}}{1-2\sqrt{\gamma}\cos\frac{r\pi}{N+1}+\gamma} \\ & \times \left\{ \sin\frac{(n+1)r\pi}{N+1} - \gamma^{-1/2}\sin\frac{nr\pi}{N+1} \right\} \\ & \times \left\{ \sin\frac{(m+1)r\pi}{N+1} - \gamma^{-1/2}\sin\frac{mr\pi}{N+1} \right\}, \quad n = 0, 1, \ldots, N. \end{aligned}$$

This can be identified with the solution of Takács [22].

We now present the results for the other cases. In all these results we use the same notation $P_n(-\beta_r)$ for the sake of brevity. We prove the result for one case. Proofs for other cases are similar.

Theorem 4. The exact transient solution for case III (i.e., $a = A + \sqrt{AB}$, $b = B + \sqrt{AB}$) is given by

$$C_{m,n}(t) = C_n + \sum_{r=1}^{N} \frac{D_{m,N} D_{N,n} P_n(-\beta_r) P_m(-\beta_r) \mathrm{e}^{-\beta_r t}}{P_N(-\beta_r) P'_{N+1}(-\beta_r)}, \quad n = 0, 1, \ldots, N,$$

where for $r = 1, 2, \ldots, N$,

$$\beta_r = A + B - 2\sqrt{AB} \cos \frac{r\pi}{N}, \tag{3.18}$$

$$P_n(-\beta_r) = \frac{(AB)^{n/2}}{\sin \frac{r\pi}{2N}} \left\{ \sin \frac{(2n+1)r\pi}{2N} - \gamma^{-1/2} \sin \frac{(2n-1)r\pi}{2N} \right\}, \tag{3.19}$$

$$P_N(-\beta_r) = (-1)^{r+2} B \left(A + \sqrt{AB}\right) (AB)^{(N-2)/2}, \tag{3.20}$$

$$\begin{aligned} P'_{N+1}(-\beta_r) = {} & \left(A + B - 2\sqrt{AB} \cos \frac{r\pi}{N}\right) (-1)^{r+2} N \left(\sqrt{AB}\right)^{N-1} \\ & \times \begin{cases} \frac{1+\cos(r\pi/N)}{\sin^2(r\pi/N)}, & r = 1, 2, \ldots, N-1, \\ (-1), & r = N, \end{cases} \end{aligned} \tag{3.21}$$

where C_n and $D_{m,n}$ are defined as in (3.17) and (2.8), respectively.

Proof. By virtue of (3.1), it is enough to find the exact expression for $P_n(-\beta_r)$, $P_N(-\beta_r)$ and $P'_{N+1}(-\beta_r)$. Substituting (3.18), $a = A + \sqrt{AB}$ and $b = B + \sqrt{AB}$ in (3.13), we get

$$\begin{aligned} P_n(-\beta_r) &= \frac{(AB)^{n/2}}{\sin \frac{r\pi}{N}} \left\{ \sin \frac{(n+1)r\pi}{N} - \left(\frac{B - \sqrt{AB}}{\sqrt{AB}}\right) \sin \frac{nr\pi}{N} \right. \\ & \qquad \left. - \left(\frac{\sqrt{AB}}{A}\right) \sin \frac{(n-1)r\pi}{N} \right\} \\ &= \frac{(AB)^{n/2}}{\sin \frac{r\pi}{N}} \left\{ \sin \frac{(n+1)r\pi}{N} + \sin \frac{nr\pi}{N} \right. \\ & \qquad \left. - \gamma^{-1/2} \left(\sin \frac{nr\pi}{N} + \sin \frac{(n-1)r\pi}{N} \right) \right\}. \end{aligned}$$

By using the trigonometric relation (3.16), we obtain (3.19). Substituting $a = A + \sqrt{AB}$ in (3.14),

$$P_N(s) = \begin{vmatrix} s+A+\sqrt{AB} & B & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ A+\sqrt{AB} & s+A+B & B & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B & B \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & A & s+A+B \end{vmatrix}_N$$

$$= \left(s+A+\sqrt{AB}\right)\prod_{k=1}^{N-1}\left(s+A+B-2\sqrt{AB}\cos\frac{k\pi}{N}\right) - B\left(A+\sqrt{AB}\right)\prod_{k=1}^{N-2}\left(s+A+B-2\sqrt{AB}\cos\frac{k\pi}{N-1}\right).$$

At the zeros of $P_{N+1}(s)$, the above equation reduces to

$$P_N(-\beta_r) = 0 - B\left(A+\sqrt{AB}\right)\left(2\sqrt{AB}\right)^{N-2}\prod_{k=1}^{N-2}\left(\cos\frac{r\pi}{N} - \cos\frac{k\pi}{N}\right).$$

We obtain (3.20) by suitably using identity (2.2) in the above equation. Finally, we find the explicit expression of $P'_{N+1}(-\beta_r)$. From (3.3), we get

$$P'_{N+1}(-\beta_r) = -\left(A+B-2\sqrt{AB}\cos\frac{r\pi}{N}\right)\prod_{\substack{k=1\\k\neq r}}^{N}\left(2\sqrt{AB}\right)\left(\cos\frac{r\pi}{N} - \cos\frac{k\pi}{N}\right).$$

When $r = N$, the above equation reduces to

$$P'_{N+1}(-\beta_N) = -\left(A+B+2\sqrt{AB}\right)\left(2\sqrt{AB}\right)^{N-1}\prod_{k=1}^{N-1}\left(-1 - \cos\frac{k\pi}{N}\right).$$

Making use of identity (2.3), we get

$$P'_{N+1}(-\beta_N) = -\left(A+B+2\sqrt{AB}\right)N\left(\sqrt{AB}\right)^{N-1}(-1)^{N+1}. \tag{3.22}$$

For the remaining $r = 1, 2, \ldots, N-1$, equation (3.3) becomes

$$P'_{N+1}(-\beta_r) = -\left(A+B-2\sqrt{AB}\cos\frac{r\pi}{N}\right)\left(2\sqrt{AB}\right)^{N-1}\left(\cos\frac{r\pi}{N}+1\right) \times \prod_{\substack{k=1\\k\neq r}}^{N-1}\left(\cos\frac{r\pi}{N} - \cos\frac{k\pi}{N}\right).$$

By making use of identity (2.3), we obtain

$$P'_{N+1}(-\beta_r) = \left(A + B - 2\sqrt{AB}\cos\frac{r\pi}{N}\right)\frac{(-1)^{r+2}N(\sqrt{AB}\,)^{N-1}\left(1+\cos\frac{r\pi}{N}\right)}{\sin^2\frac{r\pi}{N}}.$$

Combining the above result and (3.22), we get (3.21). □

Theorem 5. The exact transient solution for case II (i.e., $a = A + \sqrt{AB},\ b = B$) is given by

$$C_{m,n}(t) = C_n + \sum_{r=1}^{N}\frac{D_{m,N}D_{N,n}P_n(-\beta_r)P_m(-\beta_r)\mathrm{e}^{-\beta_r}}{P_N(-\beta_r)P'_{N+1}(-\beta_r)},\quad n = 0,1,\ldots,N,$$

where for $r = 1,2,\ldots,N$,

$$\begin{aligned}
\beta_r &= A + B - 2\sqrt{AB}\cos\frac{2r\pi}{2N+1},\\
P_n(-\beta_r) &= \frac{(AB)^{n/2}}{\sin\frac{r\pi}{2N+1}}\left\{\sin(2n+1)\frac{r\pi}{2N+1} - \gamma^{-1/2}\sin(2n-1)\frac{r\pi}{2N+1}\right\},\\
P_N(-\beta_r) &= (-1)^{r+2}B(AB)^{(N-1)/2}2\cos\frac{r\pi}{2N+1},\\
P'_{N+1}(-\beta_r) &= \frac{(2N+1)\left(A+B-2\sqrt{AB}\cos\frac{2r\pi}{2N+1}\right)(-1)^{r+2}(\sqrt{AB}\,)^{N-1}}{4\sin\frac{2r\pi}{2N+1}\sin\frac{r\pi}{2N+1}},
\end{aligned}$$

where C_n and $D_{m,n}$ are defined as in (3.17) and (2.8), respectively.

Theorem 6. The exact transient solution for case IV (i.e., $a = A - \sqrt{AB},\ b = B$) is given by

$$C_{m,n}(t) = C_n + \sum_{r=1}^{N}\frac{D_{m,N}D_{N,n}P_n(-\beta_r)P_m(-\beta_r)\mathrm{e}^{-\beta_r t}}{P_N(-\beta_r)P'_{N+1}(-\beta_r)},\quad n = 0,1,\ldots,N,$$

where for $r = 1,2,\ldots,N$,

$$\begin{aligned}
\beta_r &= A + B - 2\sqrt{AB}\cos\frac{(2r-1)\pi}{2N+1},\\
P_n(-\beta_r) &= \frac{(AB)^{n/2}}{\cos\frac{(2r-1)\pi}{2(2N+1)}}\left\{\cos\frac{(2n+1)(2r-1)\pi}{2(2N+1)} - \gamma^{-1/2}\cos\frac{(2n-1)(2r-1)\pi}{2(2N+1)}\right\},\\
P_N(-\beta_r) &= -B(AB)^{(N-1)/2}\frac{\sin\frac{(2N-1)(2r-1)\pi}{2(2N+1)}}{\sin\frac{(2r-1)\pi}{2(2N+1)}},\\
P'_{N+1}(-\beta_r) &= -\left(\sqrt{AB}\,\right)^{N-1}(2N+1)(-1)^{r+1}\frac{\left(A+B-2\sqrt{AB}\cos\frac{(2r-1)\pi}{2N+1}\right)}{4\sin\frac{(2r-1)\pi}{(2N+1)}\cos\frac{(2r-1)\pi}{2(2N+1)}},
\end{aligned}$$

where C_n and $D_{m,n}$ are defined as in (3.17) and (2.8), respectively.

Theorem 7. The exact transient solution for case V (i.e., $a = A - \sqrt{AB},\ b = B + \sqrt{AB}$) is given by

$$C_{m,n}(t) = C_n + \sum_{r=1}^{N} \frac{D_{m,N} D_{N,n} P_n(-\beta_r) P_m(-\beta_r) \mathrm{e}^{-\beta_r t}}{P_N(-\beta_r) P'_{N+1}(-\beta_r)}, \quad n = 0, 1, \ldots, N,$$

where for $r = 1, 2, \ldots, N$,

$$\beta_r = A + B - 2\sqrt{AB} \cos \frac{(2r+1)\pi}{2N+1},$$

$$P_n(-\beta_r) = \frac{(AB)^{n/2}}{\cos \frac{(2r+1)\pi}{2(2N+1)}} \left\{ \cos \frac{(2n+1)(2r+1)\pi}{2(2N+1)} - \gamma^{-1/2} \cos \frac{(2n-1)(2r+1)\pi}{2(2N+1)} \right\},$$

$$P_n(-\beta_r) = -\sqrt{AB}\left(2\sqrt{AB}\right)^{N-1} \prod_{k=1}^{N-1} \left(\cos \frac{(2r+1)\pi}{2N+1} - \cos \frac{(2k-1)\pi}{2N-1} \right) - B\left(\sqrt{AB}\right)^{N-1} \frac{\sin \frac{(2N-1)(2r+1)\pi}{2(2N+1)}}{\sin \frac{(2r+1)\pi}{2(2N+1)}},$$

$$P'_{N+1}(-\beta_r) = -\left(A + B - 2\sqrt{AB} \cos \frac{(2r+1)\pi}{2N+1} \right) \left(\sqrt{AB}\right)^{N-1} \times \begin{cases} \dfrac{(-1)^r 2^{-(N+1)} (2N+1)\left(1 + \cos \frac{(2r+1)\pi}{2N+1}\right)}{4\left(\cos \frac{(2r+1)\pi}{2N+1} - \cos \frac{\pi}{2N+1}\right) \cos \frac{(2r+1)\pi}{2(2N+1)} \sin \frac{(2r+1)\pi}{2N+1}}, & r < N, \\ \dfrac{2^{-N}(2N+1)}{-2\left(1 + \cos \frac{\pi}{2N+1}\right)}, & r = N, \end{cases}$$

where C_n and $D_{m,n}$ are defined as in (3.17) and (2.8), respectively.

4. Conclusion

Transient analysis of the master equation plays a vital role in several physical problems. The exact transient solution of the concentration of molecules in chemical kinetics of a sequence of first-order reactions with end effects is outlined. The above solution involves roots, which are found analytically in closed form irrespective of the order of matrices involved. This is in contrast with the computational difficulties encountered for some values of the parameters, because the diagonal elements of the underlying matrix become large; making the roots large and thus causing overflow while running the program.

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