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Bounds on the longest time-scale in master equations

Ulf Larsen

Physics Laboratory I, H C Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK 2100 Copenhagen Ø, Denmark

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Abstract. Exact upper and lower bounds are obtained for the class of stochastic processes described in terms of Pauli master equations with tridiagonal infinitesimal stochastic matrix. The sum of time-scales, each equal to a reciprocal eigenvalue of this matrix, is expressed in terms of the elements of arbitrary matrices. This forms the upper bound on the longest time-scale, while the same quantity, divided by the number of time-scales minus one, is the average time-scale, and forms a lower bound. The longest time-scale determines the rate of approach to equilibrium. The result is valid for any number of states, and in particular provides recurrence criteria for the infinite chain, which are consistent with known results.

1. Introduction

A wide range of physical phenomena are described in terms of the master equation in the simple form due to Pauli (cf Penrose 1979, Schnakenberg 1976). This includes processes such as relaxation, diffusion, reaction, growth, and phase transition. In most of these cases it is the longest time-scale in the model which determines the properties of most interest. On the contrary, the existing exact bounds apply to the shortest time-scale. The present work concerns exact bounds, both upper and lower, on the longest time-scale. For any master equation they may be used to estimate accurately the time needed to reach equilibrium, i.e. the rate of the processes concerned where these are determined by a long time-scale.

In § 2 we first provide definitions and mention some established properties of relevance. These are equivalent to the ergodic theorems in discrete time stochastic theory (Cox and Miller 1972, Seneta 1973). Our main result is a theorem concerning finite, tridiagonal, infinitesimal, stochastic matrices, and is obtained by recursion methods in § 3. This theorem provides the invariant coefficients of the characteristic equation in terms of the elements of the matrix. In § 4 it is applied to determine the location of the smallest eigenvalues. In the present paper this application is set in the context of systems of linear, homogeneous, first-order differential equations. In the physics literature these are most frequently referred to as the master equation (Penrose 1979, Schnakenberg 1976), while in the theory of stochastic processes (Cox and Miller 1972, Seneta 1973) they are known as the continuous time Kolmogorov equation. These equations in our case correspond to a one-dimensional arrangement of transitions between quantum states. There are models of physical relevance in this class. As far as we are aware the theorem is new. In any case, it does not appear in the standard references (such as Householder 1975, Marcus and Minc 1964, Muir 1960, Seneta 1973). Of course, recursion methods for tridiagonal matrices are well

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known (cf Cox and Miller 1972, Karlin and McGregor 1957a, b, 1958, Muir 1960) and have been applied to infinite systems, but not, to our knowledge, adapted to finite, infinitesimal, stochastic matrices, which adds an amount of complication. Neither does this theorem appear in standard applications in physics. We have applied it to Monte Carlo experiments (Larsen 1983a) and to classical diffusion in arbitrary potentials (Larsen 1983b).

2. Preliminary definitions

Let α denumerate a basis in a Hilbert space of dimension n. Let W_α denote ensemble probabilities of a system being in the pure quantum state $|\alpha\rangle$, and let

$$0 \leqslant W_\alpha \leqslant 1, \qquad \sum_{\alpha=1}^{\alpha=n} W_\alpha = 1. \tag{2.1}$$

The master equation is defined in terms of an $n \times n$ infinitesimal stochastic matrix $\boldsymbol{L}$, with elements denoted $L_{\alpha\beta}$, and forms a set of n linear, homogeneous differential equations of first order in the time t

$$\frac{\mathrm{d}W_\alpha}{\mathrm{d}t} = -\sum_{\beta=1}^{\beta=n} L_{\alpha\beta} W_\beta. \tag{2.2}$$

We assume that the matrix $\boldsymbol{L}$ does not depend on the time. This is the simplest form of the master equation and does not include memory effects.

The second part of (2.1) is satisfied if at all finite t

$$\sum_{\alpha=1}^{\alpha=n} L_{\alpha\beta} = 0. \tag{2.3}$$

Then there is at least one zero eigenvalue of $\boldsymbol{L}$. A sufficient condition for the existence of a stationary state, in which W_α^0 is a set of time independent probabilities, is that

$$\sum_{\beta=1}^{\beta=n} L_{\alpha\beta} W_\beta^0 = 0, \tag{2.4}$$

which has solutions with non-vanishing probabilities when (2.3) is assumed. Combining the two shows that the condition of detailed balance (DB)

$$L_{\alpha\beta} W_\beta^0 = L_{\beta\alpha} W_\alpha^0 \tag{2.5}$$

is also sufficient to assure the existence of such a solution. Neither of these, however, assure that the solution is unique, nor that it satisfies the bound (2.1). Keizer (1972) has shown that if

$$L_{\alpha\alpha} > 0 \quad \text{and} \quad L_{\alpha\beta} \leqslant 0, \qquad \text{for all } \alpha \neq \beta, \tag{2.6}$$

then the real parts of the eigenvalues of $\boldsymbol{L}$, denoted by l_ρ, where $\rho = 1, 2, \ldots, n$, are bounded,

$$0 \leqslant \operatorname{Re} l_\rho \leqslant 2 \max L_{\alpha\alpha}, \tag{2.7}$$

where $\max L_{\alpha\alpha}$ is the largest diagonal element of $\boldsymbol{L}$. This is a sufficient condition that the solution will satisfy (2.1), if the initial probabilities do. If all quantum states are connected by means of a chain of non-vanishing elements of $\boldsymbol{L}$, then (Schnakenberg 1976) there is only one zero eigenvalue, the stationary solution W_α^0 is unique, and reached in a finite time if n is finite. The bound (2.7) does not allow an estimate of how long this time is, as it depends on the real part, which is smallest. The solution in terms of the eigenvalues is well known. If the eigenvectors are linearly independent it has the form

$$W_\alpha = W_\alpha^0 + \sum_{\rho=2}^{\rho=n} c_{\alpha\rho}\, \mathrm{e}^{-l_\rho t}, \tag{2.8}$$

where the coefficients $c_{\alpha\rho}$ depend on the initial condition. If not, there will occur polynomials of t in their place. If the DB condition (2.5) is also assumed, then (cf § 4) all eigenvalues are real, and the solution becomes a monotonic relaxation, which can be characterised by a set of $n-1$ time-scales

$$\tau_\rho \equiv 1/l_\rho. \tag{2.9}$$

According to (2.8) then

$$(2 \max L_{\alpha\alpha})^{-1} \leqslant \tau_\rho < \infty, \tag{2.10}$$

but there is no finite upper bound. The rate determining time-scale is the largest, which we assume to be τ_2. It is, therefore, not possible on the basis of these results to assert that the equilibrium, although it exists, will be reached within times of physical relevance.

3. A theorem on the characteristic equation of certain tridiagonal matrices

Let $\boldsymbol{A}$ be a tridiagonal matrix

$$\boldsymbol{A} = \begin{pmatrix} \alpha_1 & \beta_1 & & & & \\ \gamma_1 & \alpha_2 & \beta_2 & & & \\ & \gamma_2 & \alpha_3 & \cdot & & \\ & & \cdot & \cdot & \cdot & \\ & & & \cdot & \alpha_{n-1} & \beta_{n-1} \\ & & & & \gamma_{n-1} & \alpha_n \end{pmatrix} \tag{3.1}$$

of order n, and let $\beta_n = \gamma_n \equiv 1$. For $n \geqslant 1$ the characteristic polynomial may be written in the form

$$\phi_n(\lambda) = \mathrm{Det}(\lambda \boldsymbol{I} - \boldsymbol{A}) = \sum_{m=0}^{m=n} F_n^{(m)} \lambda^m = F_n^{(0)} + F_n^{(1)}\lambda + \ldots + F_n^{(n)}\lambda^n. \tag{3.2}$$

Define

$$A_k = \frac{1}{B_k} = \prod_{\nu=1}^{k} \frac{\gamma_\nu}{\beta_\nu}, \tag{3.3}$$

$$A_0 = B_0 = 1. \tag{3.4}$$

Let

$$F_n^{(m)} \equiv \gamma_1\gamma_2 \ldots \gamma_n G_n^{(m)}, \tag{3.5}$$

$$G_n^{(0)} \equiv \begin{cases} 1 & \text{for } n = 0, \\ 0 & \text{for } n > 0. \end{cases} \tag{3.6}$$

We then prove the following theorem.

Theorem. If

$$\alpha_\nu + \gamma_\nu + \beta_{\nu-1} = 0 \qquad \text{for } 2 \leqslant \nu \leqslant n-1, \tag{3.7}$$

and

$$\alpha_1 + \gamma_1 = \alpha_n + \beta_{n-1} = 0, \tag{3.8}$$

then $G_n^{(m)}$ satisfy the recursion relations

$$G_s^{(m)} = \frac{B_s}{\beta_s} \sum_{t=m-1}^{t=s-1} \left(\sum_{k=t}^{k=s-1} A_k \right) G_t^{(m-1)} \tag{3.9}$$

for $1 \leqslant m \leqslant s \leqslant n$.

Consider first the characteristic polynomial of the principal submatrix of $\boldsymbol{A}$ of order $\nu < n$

$$\phi_\nu(\lambda) \equiv \operatorname{Det} \begin{vmatrix} \lambda - \alpha_1 & -\beta_1 & & & \\ -\gamma_1 & \lambda - \alpha_2 & -\beta_2 & & \\ & \ddots & \ddots & \ddots & \\ & & -\gamma_{\nu-2} & \lambda - \alpha_{\nu-1} & -\beta_{\nu-1} \\ & & & -\gamma_{\nu-1} & \lambda - \alpha_\nu \end{vmatrix}. \tag{3.10}$$

This is in general different from $\bar{\phi}_\nu(\lambda)$ because the elements of the last column do not satisfy (3.8). It is immediately apparent that for $\nu \geqslant 2$ there exists a recursion relation

$$\phi_\nu(\lambda) = (\lambda - \alpha_\nu)\phi_{\nu-1}(\lambda) - \beta_{\nu-1}\gamma_{\nu-1}\phi_{\nu-2}(\lambda), \tag{3.11}$$

while

$$\phi_0(\lambda) = 1, \tag{3.12}$$

$$\phi_1(\lambda) = \lambda - \alpha_1. \tag{3.13}$$

Inserting (3.7)

$$\phi_\nu(\lambda) = (\lambda + \gamma_\nu + \beta_{\nu-1})\phi_{\nu-1}(\lambda) - \beta_{\nu-1}\gamma_{\nu-1}\phi_{\nu-2}(\lambda). \tag{3.14}$$

If $\nu = n$, according to (3.8), we would rather have

$$\bar{\phi}_n(\lambda) = (\lambda + \beta_{n-1})\phi_{n-1}(\lambda) - \beta_{n-1}\gamma_{n-1}\phi_{n-2}(\lambda). \tag{3.15}$$

Hence

$$\phi_n(\lambda) = \bar{\phi}_n(\lambda) + \gamma_n\phi_{n-1}(\lambda). \tag{3.16}$$

Inserting this repeatedly in the right-hand side of (3.15) gives

$$\begin{aligned} \bar{\phi}_n(\lambda) &= (\lambda + \beta_{n-1})\bar{\phi}_{n-1}(\lambda) + \lambda\gamma_{n-1}\phi_{n-2}(\lambda) \\ &= \beta_{n-1}\bar{\phi}_{n-1}(\lambda) + \lambda[\bar{\phi}_{n-1}(\lambda) + \gamma_{n-1}\bar{\phi}_{n-2}(\lambda) + \gamma_{n-1}\gamma_{n-2}\bar{\phi}_{n-3}(\lambda) + \dots \\ &\quad + \gamma_{n-1} \dots \gamma_2\phi_1(\lambda)] \end{aligned} \tag{3.17}$$

for $n \geqslant 3$. ϕ_1 is given by (3.13) and (3.8)

$$\phi_1(\lambda) = \lambda + \gamma_1 = \bar{\phi}_1(\lambda). \tag{3.18}$$

Hence $\bar{\phi}_\nu$ for $\nu < n$ are the characteristic polynomials of the matrix which would have corresponded to ν being the last column and the elements of this column satisfying (3.8) instead of (3.7). Adding all rows of the determinant of $\bar{\phi}_n(x)$ to the first row, by (3.7), produces λ in all the positions in the first row. Hence $\bar{\phi}_n$ contains a factor λ for all $n \geq 2$, which corresponds to an eigenvalue zero. Thus

$$F_n^{(0)} = 0 \qquad \text{for } n \geq 2, \tag{3.19}$$

and of course

$$F_1^{(0)} = -\alpha_1 = \gamma_1. \tag{3.20}$$

Now define polynomials

$$F_n^{(m)}(\lambda) \tag{3.21}$$

by putting

$$\bar{\phi}_n(\lambda) \equiv F_n^{(0)} + \lambda F_n^{(1)}(\lambda) \tag{3.22}$$

and in general, for $1 \leq m \leq n-1$,

$$F_n^{(m)}(\lambda) = F_n^{(m)} + \lambda F_n^{(m+1)}(\lambda). \tag{3.23}$$

Here

$$F_n^{(m)}(0) \equiv F_n^{(m)}, \tag{3.24}$$

and

$$F_n^{(n)}(\lambda) = F_n^{(n)} = 1. \tag{3.25}$$

Inserting in (3.17), using (3.19), and cancelling an overall factor of λ then gives, for $n \geq 3$,

$$F_n^{(1)}(\lambda) = \beta_{n-1}F_{n-1}^{(1)}(\lambda) + \lambda F_{n-1}^{(1)}(\lambda) + \lambda\gamma_{n-1}F_{n-2}^{(1)}(\lambda) + \ldots + \lambda\gamma_{n-1}\ldots\gamma_3 F_2^{(1)}(\lambda)$$
$$+ \lambda\gamma_{n-1}\ldots\gamma_2 + \gamma_{n-1}\gamma_{n-2}\ldots\gamma_2\gamma_1. \tag{3.26}$$

Setting $\lambda = 0$ gives, according to (3.24),

$$F_n^{(1)} = \beta_{n-1}F_{n-1}^{(1)} + \gamma_{n-1}\ldots\gamma_1. \tag{3.27}$$

Repeating the process, by inserting (3.23) in (3.26), using (3.27) to cancel terms independent of λ, then gives subsequently

$$F_n^{(2)} = \beta_{n-1}F_{n-1}^{(2)} + F_{n-1}^{(1)} + \gamma_{n-1}F_{n-2}^{(1)} + \ldots + \gamma_{n-1}\ldots\gamma_3 F_2^{(1)} + \gamma_{n-1}\ldots\gamma_2. \tag{3.28}$$

By (3.25) $F_1^{(1)} = 1$, so

$$F_n^{(2)} = \beta_{n-1}F_{n-1}^{(2)} + \sum_{t=1}^{n-1} F_t^{(1)} \frac{\prod_{\nu=1}^{n-1}\gamma_\nu}{\prod_{\nu=1}^{t}\gamma_\nu}. \tag{3.29}$$

Proceeding to the mth term

$$F_n^{(m)} = \beta_{n-1}F_{n-1}^{(m)} + \sum_{t=m-1}^{n-1} F_t^{(m-1)} \frac{\prod_{\nu=1}^{n-1}\gamma_\nu}{\prod_{\nu=1}^{t}\gamma_\nu}. \tag{3.30}$$

This follows since the string of $F_t^{(m-1)}$ will always terminate with the $F_{m-1}^{(m-1)} = 1$, which may be regarded as multiplying the last string of $\gamma_{n-1}\ldots\gamma_m$. When $m = n$, according to (3.23) and (3.25), the first term on the right-hand side is absent, while the sum only contains one term. Hence

$$F_n^{(n)} = F_{n-1}^{(n-1)}, \tag{3.31}$$

which is consistent with (3.25). The solution of (3.30) is (see e.g. Bender and Orszag 1978)

$$F_n^{(m)}=\left(\prod_{\nu=1}^{n-1}\beta_\nu\right)\sum_{k=m-1}^{n-1}\sum_{t=m-1}^{k}F_t^{(m-1)}\frac{\prod_{\nu=1}^{k}\gamma_\nu}{\prod_{\nu=1}^{t}\gamma_\nu}\frac{1}{\prod_{\nu=1}^{k}\beta_\nu} \tag{3.32}$$

using (3.31) as boundary condition at $m=n$. Using (3.5) this becomes

$$G_n^{(m)}=\frac{B_n}{\beta_n}\sum_{k=m-1}^{n-1}\sum_{t=m-1}^{k}G_t^{(m-1)}A_k. \tag{3.33}$$

By the equivalence of the sums

$$\sum_{k=m-1}^{n-1}\sum_{t=m-1}^{k}\cdots=\sum_{t=m-1}^{n-1}\sum_{k=t}^{n-1}\cdots \tag{3.34}$$

this produces the recursion (3.9).

It remains to show how to start the recursion for $m=1$. From (3.27)

$$F_n^{(1)}=\left(\prod_{\nu=2}^{n-1}\beta_\nu\right)\left(\sum_{k=2}^{n-1}\frac{\prod_{\nu=1}^{k}\gamma_\nu}{\prod_{\nu=2}^{k}\beta_\nu}+F_2^{(1)}\right). \tag{3.35}$$

According to (3.2), (3.7) and (3.8)

$$\bar{\phi}_2(\lambda)=\lambda(F_2^{(1)}+\lambda F_2^{(2)})=(\lambda-\alpha_1)(\lambda-\alpha_2)-\beta_1\gamma_1=\lambda^2-\lambda(\alpha_1+\alpha_2). \tag{3.36}$$

Hence

$$F_2^{(2)}=1, \tag{3.37}$$

$$F_2^{(1)}=-(\alpha_1+\alpha_2)=\gamma_1+\beta_1. \tag{3.38}$$

So

$$F_n^{(1)}=\left(\prod_{\nu=1}^{n-1}\beta_\nu\right)\sum_{k=2}^{n-1}\frac{\prod_{\nu=1}^{k}\gamma_\nu}{\prod_{\nu=1}^{k}\beta_\nu}+\left(\prod_{\nu=1}^{n-1}\beta_\nu\right)\left(1+\frac{\gamma_1}{\beta_1}\right), \tag{3.39}$$

$$G_n^{(1)}=\frac{B_n}{\beta_n}\left(\sum_{k=2}^{n-1}A_k+1+\frac{\gamma_1}{\beta_1}\right)=\frac{B_n}{\beta_n}\sum_{k=0}^{n-1}A_k. \tag{3.40}$$

As this is generated by starting with (3.6) in (3.9) the proof of the theorem is complete.

4. Results

The invariant coefficients of the characteristic polynomial (3.2) may be expressed in terms of the eigenvalues. It is straightforward to obtain by means of the recursion

$$F_n^{(n-1)}=-\mathrm{Tr}(\boldsymbol{L})=-\sum_\rho l_\rho. \tag{4.1}$$

Since $l_1=0$ we have

$$F_n^{(0)}=(-1)^n\,\mathrm{Det}(\boldsymbol{L})=(-1)^n\prod_{\rho=1}^{\rho=n}l_\rho=0, \tag{4.2}$$

and the next in order are

$$F_n^{(1)} = (-1)^{n-1} \prod_{\rho=2}^{\rho=n} l_\rho, \tag{4.3}$$

$$F_n^{(2)} = (-1)^{n-2} \sum_{\rho=2}^{\rho=n} \frac{l_2 l_3 \ldots l_n}{l_\rho}. \tag{4.4}$$

These give the sum of the time-scales

$$\tau \equiv \sum_{\rho=2}^{\rho=n} \tau_\rho = \sum_{\rho=2}^{\rho=n} \frac{1}{l_\rho} = \sum_{\rho=2}^{\rho=n} \frac{\prod_{\rho'=2} l_{\rho'}}{l_\rho} \Big/ \prod_{\rho'=2} l_{\rho'} = -\frac{F_n^{(2)}}{F_n^{(1)}}. \tag{4.5}$$

From (3.9), for $1 \leqslant s \leqslant n$,

$$G_s^{(1)} = \frac{B_s}{\beta_s} \sum_{t=0}^{t=s-1} \left(\sum_{k=t}^{k=s-1} A_k \right) G_t^{(0)} = \frac{B_s}{\beta_s} \sum_{k=0}^{k=s-1} A_k, \tag{4.6}$$

and next

$$G_n^{(2)} = \frac{B_n}{\beta_n} \sum_{s=1}^{s=n-1} \left(\sum_{k=s}^{k=n-1} A_k \right) G_s^{(1)} = \frac{B_n}{\beta_n} \sum_{s=1}^{s=n-1} \left(\sum_{k=s}^{k=n-1} A_k \right) \frac{B_s}{\beta_s} \left(\sum_{l=0}^{l=s-1} A_l \right). \tag{4.7}$$

Defining

$$J_s \equiv \sum_{k=0}^{k=s-1} A_k, \tag{4.8}$$

we have, using the definition (3.3) and (3.5),

$$\tau = -\sum_{s=1}^{s=n-1} \frac{(J_n - J_s) J_s}{\beta_s A_s J_n}. \tag{4.9}$$

In terms of the elements of the tridiagonal $\boldsymbol{L}$

$$A_k = \prod_{\nu=1}^{\nu=k} \frac{L_{\nu+1,\nu}}{L_{\nu,\nu+1}}. \tag{4.10}$$

If all the off-diagonal elements are negative, according to (2.6), then τ is non-negative, in agreement with (2.10). In any case, τ is real, the eigenvalues occur in complex conjugate pairs.

Let us define an average relaxation time by

$$\bar{\tau} \equiv \frac{1}{n-1} \sum_{\rho=2}^{\rho=n} \tau_\rho = \frac{\tau}{n-1}, \tag{4.11}$$

and let us assume the time-scales are arranged in order of magnitude

$$\operatorname{Re} \tau_2 \geqslant \operatorname{Re} \tau_3 \geqslant \ldots \geqslant \operatorname{Re} \tau_n. \tag{4.12}$$

Under the condition (2.6) all these are positive, so

$$\operatorname{Re} \tau_2 \leqslant \tau \leqslant (n-1) \operatorname{Re} \tau_2. \tag{4.13}$$

Consequently, the largest time-scale is bounded as follows:

$$\bar{\tau} \leqslant \operatorname{Re} \tau_2 \leqslant \tau. \tag{4.14}$$

The lower bound is sharper than (2.10) since

$$(2 \max L_{\alpha\alpha})^{-1} \leq \operatorname{Re} \tau_n \leq \bar{\tau}. \tag{4.15}$$

An upper bound has not been established before. When the longest time-scale Re τ_2 becomes much larger than all the others the lower bound becomes much better than (2.10), and for finite n it is of the same order as the upper bound in the quantity that becomes large.

If a link in the chain of matrix elements is broken by letting a pair become zero, then τ becomes infinite, in agreement with the existence of a second zero eigenvalue. The two segments can be considered as above, and may have different time-scales. This case presents no loss of generality.

If the DB condition is also assumed, then there exists an orthogonal transformation matrix $\boldsymbol{U}$, with elements

$$U_{\alpha\beta} = \delta_{\alpha\beta}/\sqrt{W_\alpha^0}, \tag{4.16}$$

whereby $\boldsymbol{L}$ is similar to a symmetric matrix $\boldsymbol{M}$, with elements

$$M_{\alpha\beta} = L_{\alpha\beta}(W_\beta^0 / W_\alpha^0)^{1/2} = L_{\beta\alpha}(W_\alpha^0 / W_\beta^0)^{1/2} = M_{\beta\alpha}. \tag{4.17}$$

The eigenvalues are therefore real. In this case we may simplify the expressions. We get

$$A_k = \prod_{\nu=1}^{\nu=k} \frac{W_{\nu+1}^0}{W_\nu^0} = \frac{W_{k+1}^0}{W_1^0}. \tag{4.18}$$

Define $J_0 \equiv 0$

$$H_{s,t} \equiv W_1^0 (J_t - J_s) = \sum_{k=s+1}^{k=t} W_k^0. \tag{4.19}$$

Then, in terms of the elements of $\boldsymbol{L}$ or $\boldsymbol{M}$,

$$\tau = -\sum_{s=1}^{s=n-1} \frac{H_{0,s} H_{s,n}}{L_{s,s+1} W_{s+1}^0} = -\sum_{s=1}^{s=n-1} \frac{H_{0,s} H_{s,n}}{M_{s,s+1} (W_s^0 W_{s+1}^0)^{1/2}}. \tag{4.20}$$

For real time-scales the bounds become

$$(2 \max L_{\alpha\alpha})^{-1} \leq \tau_n \leq \bar{\tau} \leq \tau_2 \leq \tau, \tag{4.21}$$

where τ_2 is the largest time and τ_n is the smallest time. The sums present no computational problems.

For infinitely large n the model corresponds to the birth-and-death problem. In this case the conclusions about the possibilities of reaching the equilibrium may not apply, but we can use the bounds on Re τ_2 to investigate the possibilities. If τ, and consequently Re τ_2, remains finite, then equilibrium can be reached in a finite time. If $\bar{\tau}$ diverges, then so does Re τ_2, and equilibrium cannot be reached in a finite time. The behaviour of τ depends on the function J_s, defined by (4.8) and (3.3) in terms of the matrix elements. This is finite and non-negative by definition of the model, now including (2.6), but not necessarily DB. For $1 \leq s \leq n-1$ $J_s < J_n$. From (4.9)

$$\tau = \sum_{s=1}^{s=n-1} \frac{J_s}{|\beta_s| A_s} \left(1 - \frac{J_s}{J_n}\right) < \sum_{s=1}^{s=n-1} \frac{J_s}{|\beta_s| A_s}. \tag{4.22}$$

Consequently τ is finite, and equilibrium reached in a finite time of the order Re τ_2, provided the infinite sum is convergent,

$$\sum_{s=1}^{\infty} \frac{J_s}{|\beta_s| A_s} < \infty. \tag{4.23}$$

Karlin and McGregor (1957a, b, 1958) showed that the stochastic process is null-recurrent if and only if

$$\sum_{s=1}^{\infty} \frac{1}{|\beta_s| A_s} = \infty \qquad \text{and} \qquad \lim J_n = \infty. \tag{4.24}$$

We conclude null-recurrence from the bounds (4.21) if for $n \to \infty$

$$\lim \frac{1}{n-1} \sum_{s=1}^{s=n-1} \frac{J_s}{|\beta_s| A_s} \left(1 - \frac{J_s}{J_n}\right) = \infty. \tag{4.25}$$

Under the condition of DB the J_s must all be finite, as the J_n is the sum of probabilities in (2.1) divided by W_1^0. Otherwise this need not be the case.

The simplest model of diffusion corresponds to equal matrix elements

$$\beta_\nu = \gamma_\nu = \beta. \tag{4.26}$$

We get $A_k = 1$ for all k, and $J_s = s$. Hence

$$\tau = \frac{1}{|\beta|} \sum_{s=1}^{s=n-1} \frac{(n-s)s}{n} = \frac{1}{6|\beta|} (n-1)(n+1), \tag{4.27}$$

$$\bar{\tau} = (1/6|\beta|)(n+1). \tag{4.28}$$

Since both diverge for $n \to \infty$ no equilibrium is ever reached. The diffusion process is null-recurrent, as its mean recurrence time is infinite.

5. Conclusions

We have considered the class of models described in terms of master equations with constant, tridiagonal infinitesimal stochastic matrix $\boldsymbol{L}$. Despite its simplicity, this equation is of considerable physical relevance. We obtained exact upper and lower bounds on the longest time-scale, expressed in terms of the elements of $\boldsymbol{L}$ for arbitrary models in this class. It then becomes possible to determine explicitly the rate controlling time-scale in all processes of this kind, whereas it has previously only been possible to construct a lower bound on the fastest time-scale, which has no such significance. The results apply to any number n of pure quantum states, and are easily computable. In particular, statements about the recurrence properties in models with n infinite can be constructed on the basis of an analysis of the convergence properties of the bounds.

The bounds are both proportional to the sum of time-scales, and are therefore both proportional to the mean time-scale $\bar{\tau}$, for which an exact expression is given. If the principle of detailed balance is introduced in the matrix $\boldsymbol{L}$ it becomes possible to express these quantities in terms of the equilibrium probabilities. This opens up the possibility of numerous applications in quantum and classical statistical mechanics. Some examples are discussed in Larsen (1983a, b).

The standard theorems on the location of the eigenvalues of matrices (cf Marcus and Minc 1964, Muir 1960) concern the complete spectrum. They do not provide information about the separation of eigenvalues within the spectrum. This may also be said of the ergodic theorems of stochastic theory, which are obtained from the Perron–Frobenius theorem (Seneta 1973). These concern the conditions that the unit eigenvalue is simple, and are equivalent to statements about the zero eigenvalue in the continuous time models (Keizer 1972, Schnakenberg 1976). Although these theorems may show that the infinite time limit provides a unique equilibrium state, if $\boldsymbol{L}$ is irreducible as we also assume here, they do not determine how long it will take. This requires a statement about the next-to-smallest eigenvalues in the spectrum, the smallest being zero. For any infinitesimal stochastic matrix these are inside the spectrum, and the zero eigenvalue keeps all general bounds equal to zero (cf § 2) and therefore useless for this purpose. This presents a problem which, to our knowledge was not addressed before, at least not in the present context. Because of this we have not found earlier work which could be of assistance in constructing a shorter proof than the one given in § 3, which relies entirely on elementary algebra.

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