Limiting Conditional Distributions for a Class of Autocatalytic Chemical Reactions

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The Problem
We consider the problem of describing the evolution over time of the number of molecules of the autocatalyst X in the chemical system

$$A + X \xrightarrow{k_{b}} 2X$$

$$X \xrightarrow{k_i} B.$$  

The reaction system is assumed to be open with respect to A and B, that is molecules of A and B are free to enter and leave the reaction vessel at any time. The effect of this is that the concentrations and therefore the number of molecules of A and B are constant. We denote this constant quantity of A by \(a\). Note also that if the autocatalyst X is exhausted, the reaction ceases.

To model the number of molecules of X we use a birth-death process. As usual for birth-death processes, we write the transition rate out of state \(i\) being in state \(i\) as \(q_i = k_{b} + k_{i}i(i - 1)/2\).

Figure 1 demonstrates the typical behaviour of the process:

Limiting Conditional Distributions

In a 1987 paper, Parsons and Pollett [4] use the idea of a quasistationarity to describe this behaviour, this approach considers the limiting conditional distribution

$$m_j = \lim_{i \to \infty} \Pr(X(t) = j | X(0) \neq 0, X(0) = i).$$

The quantity \(m_j\) gives the limiting probability of the system being in state \(j\), given that the reaction has not yet stopped.

When it exists, the limiting conditional distribution (LCD) is given by the solution of the eigenvector equations

$$\sum_{j \in C} m_j q_{ij} = -\nu \alpha_s m_i, \quad i \in C,$$

for the maximal positive value \(\nu\) of \(\nu\) for which a non-negative solution exists. Here \(Q = (q_{ij}, i, j \in S)\) is the matrix of transition rates, with the convention that the diagonal element \(q_i\) is set to \(-q_i\), where \(q_i = \sum_{j \in C \setminus \{0\}} q_{ij}\) is the total rate out of state \(i\). It is pertinent to note that when \(C\) is finite we are guaranteed (by Perron-Frobenius theory) that there exists \(\nu > 0\) such that (1) has a positive solution.

Parsons and Pollett use various techniques for approximating the LCD without establishing its existence.

Birth-Death Processes

The simple structure of birth-death processes means that they submit to analysis rather more easily than more general processes. As usual for birth-death processes, we write \(\lambda_i, i, j \in S\) and \(\mu_j = q_{ij}, i, j \in S\) for the birth and death rates, and \(\pi_i = 1, i \geq 0\) for the potential coefficients.

Theorem (van Doorn [5]): If the series

$$D = \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \sum_{m=0}^{n} \pi_m$$

converges, then there exists a unique \(\nu > 0\) such that (1) has a non-negative solution \(m\).

Truncation Approximation

Having established the existence of a LCD, i.e. a finite measure \(m\) such that \(\sum_{j \in C} m_j q_{ij} = -\nu \alpha_s m_i, \quad j \in C\), we wish to consider whether we can approximate \(m\) numerically by using sufficiently large finite truncations of the system. In other words, we wish to investigate the convergence of the solutions \(m^{(n)}\) of

$$\sum_{j \in C^{(n)}} m_j^{(n)} q_{ij}^{(n)} = -\nu \alpha_s m_i^{(n)}, \quad j \in C^{(n)}.$$

where \(C^{(n)}\) is a sequence of successively larger finite truncations of \(C\). We are guaranteed that such solutions exist because each \(C^{(n)}\) is a finite set.

As well as not establishing the existence of a limiting conditional distribution, Parsons and Pollett neglected to verify the validity of the truncation techniques which they used.

Lemma (Breyer and Hart [1]): If a LCD exists for the finite state space model then the eigenvalues \(\nu^{(n)}\) of the finite truncation converge to \(\nu\); in fact

$$\nu^{(n)} \to \nu \quad \text{as} \quad n \to \infty.$$

This lemma tells us that we only need to worry about the convergence of the eigenvectors \(m^{(n)}\). In addition to the above lemma, Breyer and Hart [1] also provide some sufficient conditions which ensure both that the sequence \(m^{(n)}\) converges and that it in fact converges to the limiting conditional distribution \(m\). In the special case of birth-death processes however, the solution to this problem has been known for some time:

Proposition (Hart [2], Theorem 5.7): If a LCD exists for an infinite state space birth-death process, then the finite approximations \(m^{(n)}\) converge to the LCD \(m\), in the sense that

$$\lim_{n \to \infty} m^{(n)} = m.$$

So if the chemical system has a limiting conditional distribution, Parsons and Pollett’s approximation methods are valid.

References


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