

Quantum Techniques for Studying Equilibrium in Reaction Networks

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Abstract

Anderson, Craciun, and Kurtz have proved that a stochastically modelled chemical reaction system with mass-action kinetics admits a stationary distribution when the deterministic model of the same system with mass-action kinetics admits an equilibrium solution obeying a certain ‘complex balance’ condition. Here we present a proof of their theorem using tools from the theory of second quantization: Fock space, annihilation and creation operators, and coherent states. This is an example of ‘stochastic mechanics’, where we take techniques from quantum mechanics and replace amplitudes by probabilities. We explain how the systems studied here can be described using either of two equivalent formalisms: reaction networks, as in chemistry, or stochastic Petri nets, as in some other disciplines.

1 Introduction

Systems with uncertainty are often modelled in two ways. The first of these is via the deterministic evolution of the expected state of the system. The second, more detailed approach describes the time evolution of a probability distribution or quantum state. Often the second approach reduces to the first in a suitable limit.

One prominent class of systems modelled in both ways are field theories, which come in both classical and quantum versions. Another class of such systems are chemical reactions. Chemists describe the time evolution of chemical concentrations in a deterministic way using *rate equations*, but they also describe interactions between chemical species stochastically, using *master equations*.

In this paper we aim to demonstrate the analogy between quantum field theory and chemistry, casting our discussion of chemical master equations in the language of Fock space and creation and annihilation operators. This work is part of a broader program emphasizing the links between quantum mechanics and a subject we call ‘stochastic mechanics’, where probabilities replace amplitudes [5, 6, 4].

Using second quantization methods to model classical systems goes back to Doi [7], and was developed further by Grassberger and Scheunert [11], among others. However, there is an extensive line of work in mathematical chemistry that does not use these techniques, but might profit from them. To illustrate how they work, we use them here to provide a new, compact proof of a theorem

by Anderson, Craciun, and Kurtz [1]. This theorem says that under certain assumptions, equilibrium solutions of deterministic evolution equations give equilibrium solutions of stochastic ones.

Chemists specify both the rate equation and the master equation starting from a ‘reaction network’. The language of Petri nets is equivalent to that of reaction networks, but more widely used beyond discussions of chemistry. In particular, stochastic Petri nets are used in systems biology, epidemiology, and ecology [9, 13, 14, 17]. Unfortunately, results proved in one language are not instantly accessible to researchers only familiar with the other. Thus, we start by explaining how to translate between reaction networks and Petri nets. Keeping this in mind, it becomes clear that the Anderson–Craciun–Kurtz theorem is not merely a result about chemical reactions: it applies to a wide class of stochastic systems.

2 Reaction networks and Petri nets

Reaction networks model the salient chemical interactions in an isolated chemical system. These networks, first defined by Aris [3], consist of a set of chemical species together with a set of reactions that may take place among them. More precisely:

Definition 1. A reaction network (S, K, T, s, t) consists of:

- a finite set S ,
- a finite set K of multisets with elements in S ,
- a finite set T ,
- functions $s, t: T \rightarrow K$.

We call the elements of S **species**, those of K **complexes**, and those of T **reactions**. We call $s(\tau)$ and $t(\tau)$ the **reactants** and **products** of the reaction $\tau \in T$ respectively.

We should note that chemists use the term ‘chemical reaction network’. While chemists call the elements of T ‘reactions’, the Petri net literature uses the term ‘transitions’ for essentially the same thing. We often write complexes as linear combinations of elements of S with natural number coefficients, writing for example the multiset $\{A, A, B\}$ as $2A + B$. If a reaction $\tau \in T$ has the complex κ as its reactants and κ' as its products, we write $\tau: \kappa \rightarrow \kappa'$.

Reaction networks admit a useful and easy-to-read representation as directed graphs, with K as the set of vertices, and a directed edge from the complex $a \in K$ to the complex $b \in K$ for each reaction with a as its reactants and b as its products. For example, consider the reaction network with

$$S = \{A, B, C, AC\}$$

as its set of species,

$$K = \{\emptyset, A, B, AC, A + C, 2B + C\}$$

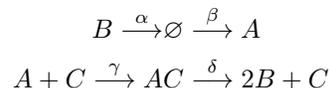
as its set of complexes, and with four reactions

$$R = \{\alpha, \beta, \gamma, \delta\}$$

such that

$$\begin{aligned} \alpha: \emptyset &\rightarrow A \\ \beta: B &\rightarrow \emptyset \\ \gamma: A + C &\rightarrow AC \\ \delta: AC &\rightarrow 2B + C \end{aligned}$$

This reaction network describes the transformation of one molecule of species A into two of species B with the help of the catalyst C , in a system where A is replenished and B is consumed. It may be pictured as this graph:



In general, the graph conveys all the information in the reaction network, except when there are species that do not appear in any complex. The graph may have multiple edges or self-loops. It is thus the kind of graph sometimes called a ‘directed multigraph’ or ‘quiver’. These terms may obscure the simplicity of the concept, so for the purposes of this paper we simply say:

Definition 2. A **graph** consists of a set E of **edges**, a set V of **vertices**, and **source and target maps** $s, t: E \rightarrow V$.

A reaction network is thus equivalent to a finite set S of species, a finite set K of multisubsets of S , and a graph with K as its set of vertices and some finite set R of edges.

An equivalent framework for describing chemical processes, now used more generally to describe concurrent processes across a wide variety of sciences, is that of Petri nets [16].

Definition 3. A **Petri net** (S, T, i, o) consists of:

- a finite set S ,
- a finite set T ,
- functions $i, o: S \times T \rightarrow \mathbb{N}$.

We call the elements of S **species** and those of T **transitions**. We think of i and o as specifying the number of each species appearing as the **inputs** and **outputs** respectively to each transition.

In the Petri net literature the species are often called ‘places’. For convenience we shall often write $k = |S|$ for the number of species present in a Petri net, and identify the set S with the set $\{1, \dots, k\}$.

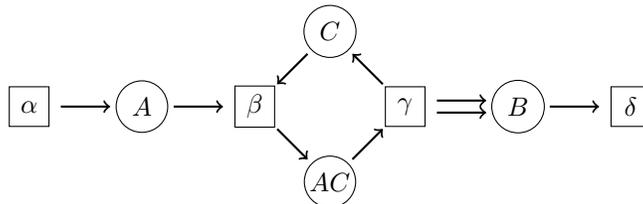
Each reaction network may be considered as equivalent to some Petri net. Here the set of species of the Petri net is the same as that of the equivalent reaction network. The set of transitions of the Petri net corresponds to the set of reactions of the reaction network. The input and output functions of each transition respectively specify the number of times each species appears as a reactant and product of the corresponding reaction. For example, the above example of a reaction network is equivalent to the Petri net with

$$\begin{aligned} S &= \{A, B, C, AC\}, \\ T &= \{\alpha, \beta, \gamma, \delta\}, \end{aligned}$$

the input function $i: S \times T \rightarrow \mathbb{N}$ taking value 1 on the pairs (A, β) , (C, β) , (AC, γ) and value 0 otherwise, and the output function $o: S \times T \rightarrow \mathbb{N}$ taking value 1 on (A, α) and (AC, β) , value 2 on (B, γ) , and value 0 otherwise.

Petri nets are also commonly represented as graphs, although not in the same way as their equivalent reaction networks. In this case we draw a graph whose set of vertices is $S \cup T$, with precisely $i(j, \tau)$ directed edges drawn from the species $j \in S$ to the transition $\tau \in T$, and precisely $o(j, \tau)$ directed edges drawn from the transition $\tau \in T$ to the species $j \in S$. So, this graph is ‘bipartite’: there are no edges going between two vertices that both represent states, and no edges going between two vertices that both represent transitions.

Our example Petri net is represented by this graph:



Note that there are two edges from γ to B , as the transition γ produces two instances of species B .

3 Stochastic Petri nets with mass-action kinetics

It is often useful to talk of the amount of each chemical present in a chemical system at a given time. The possible amounts are represented by what are termed the ‘states’ of a Petri net. By a **pure state** of a Petri net we refer to a vector $x \in \mathbb{N}^k$ with i th entry x_i specifying the number of instances of the i th species. This generalises in two ways. First, we define a **classical state** to be any vector $x \in [0, \infty)^k$ of nonnegative real numbers, and think of such a state as specifying an expected number or concentration of the species present. Second, we define a **mixed state** to be a probability distribution ψ over the pure states of the Petri net. Of great interest is how states—of both generalized types—evolve or change over time.

In modelling the evolution of the state of a Petri net, we must first specify a kinetics for the system. In this paper we consider systems that evolve by the law of mass action [12]. Very roughly, this law states that the rate at which a transition occurs is proportional to the product of the concentrations of all its input species. We call the constant of proportionality for each transition its ‘rate constant’. A Petri net where each transition has a rate constant is called a ‘stochastic Petri net’:

Definition 4. A **stochastic Petri net** (S, T, i, o, r) consists of a Petri net (S, T, i, o) together with a function $r: T \rightarrow (0, \infty)$ specifying a **rate constant** for each transition.

Just as Petri nets are equivalent to reaction networks, a stochastic Petri net is equivalent to a **stochastic reaction network**, meaning a reaction network together with a rate constant for each reaction.

A stochastic Petri net gives rise to an evolution principle for each of our generalized notions of state above. The ‘rate equation’ describes the system with continuous parameters changing in a deterministic way, saying how a classical state changes with time. On the other hand, the ‘master equation’ describes the system with a mixed state—a probability distribution over the pure states of the system—and treats the evolution of pure states as a stochastic process, saying how this probability distribution changes with time.

The master equation is more fundamental. It plays a role similar to the equations of quantum electrodynamics, which describe the amplitudes for creating and annihilating individual photons. The rate equation is less fundamental: it resembles the classical Maxwell equations, which describe changes in the electromagnetic field in a deterministic way. The classical Maxwell equations are an approximation to quantum electrodynamics which becomes good in a certain ‘classical limit’ where there are many photons in each state. Similarly, although the rate equation and master equation describe distinct notions of evolution, under certain conditions the rate equation can be derived from the master equation in the limit where the number of things of each species become large, and the uncertainty in these numbers becomes negligible [2, 4]. In this case taking the expected value of an equilibrium solution for the master equation gives an equilibrium solution of the rate equation.

The Anderson–Craciun–Kurtz theorem shows that in some cases the converse holds too: from an equilibrium solution of the rate equation we can sometimes construct an equilibrium solution of

the master equation. Remarkably, this solution is precise rather than approximate—and it is given by a simple formula.

The rate equation

Let (S, T, i, o, r) be a stochastic Petri net with $k = |S|$ species. For each species $j \in S$ and transition $\tau \in T$, write $s_j(\tau) = i(j, \tau)$ for the number of times the species j appears as an input to the transition τ , and similarly write $t_j(\tau) = o(j, \tau)$ for the number of times it appears an output. We thus have vectors

$$s(\tau) = (s_1(\tau), \dots, s_k(\tau)) \in \mathbb{N}^k$$

and

$$t(\tau) = (t_1(\tau), \dots, t_k(\tau)) \in \mathbb{N}^k$$

describing the reactants and products of the transition τ .

The rate equation models the time evolution of a classical state of a stochastic Petri net in a deterministic way. According to the deterministic law of mass action, for each transition τ the rate of change of x is the product of:

- the change $t(\tau) - s(\tau)$ in numbers of each species due to τ ;
- the concentration of each input species i of τ raised to the power given by the number of times it appears as an input, namely $s_i(\tau)$;
- the rate constant $r(\tau)$ of τ .

Definition 5. *The rate equation for a stochastic Petri net (S, T, i, o, r) is*

$$\frac{d}{dt}x(t) = \sum_{\tau \in T} r(\tau)(t(\tau) - s(\tau))x(t)^{s(\tau)},$$

where $x: \mathbb{R} \rightarrow [0, \infty)^k$ and we have used multi-index notation to define

$$x^{s(\tau)} = x_1^{s_1(\tau)} \dots x_k^{s_k(\tau)}.$$

We will in particular concern ourselves with states $c \in [0, \infty)^k$ for which $x(t) = c$ for all $t \in \mathbb{R}$ is a solution of the rate equation. In such a state the rate equation says that the net rate of production of each species is zero. We call such a state an **equilibrium solution** of the rate equation.

Second quantization and the master equation

Modelling the evolution of a mixed state is a bit more involved, and here methods from quantum mechanics provide an interesting perspective. Following second quantization techniques used in quantum field theory, we begin our discussion by introducing a power series notation to describe the mixed states of a stochastic Petri net, and then creation and annihilation operators to describe how these mixed states may evolve. This will allow us to give a compact expression of the master equation.

Fix some mixed state. For each $n \in \mathbb{N}^k$, let ψ_n be the probability that for each i we have exactly $n_i \in \mathbb{N}$ of the i th species present in this mixed state. We then express this mixed state as a formal power series in some formal variables z_1, \dots, z_k , with the coefficient of

$$z^n = z_1^{n_1} \dots z_k^{n_k}$$

being the probability ψ_n . That is, we write our mixed state as $\Psi = \sum_{n \in \mathbb{N}^k} \psi_n z^n$. Note that as Ψ represents a mixed state, and a mixed state is a probability distribution, the coefficients ψ_n of must

sum to 1. Indeed, the mixed states are precisely the formal power series Ψ with coefficients summing to 1. The simplest examples of states are the monomials $z^n = z_1^{n_1} \cdots z_k^{n_k}$; these are the pure states.

The simplest changes to the state of a Petri net are the addition, or creation, of a new instance of the i th species, and the removal, or annihilation, of an existing instance of the i th species. Moreover, all changes of state can be seen as sequences of such operations. To provide notation for processes on mixed states, we thus define creation and annihilation operators on formal power series. These definitions are inspired by their analogues in quantum field theory. Our notation here follows that used there directly, where the creation and annihilation operators may be seen as adjoint linear operators.

Let $1 \leq i \leq k$. The **creation operator** a_i^\dagger of the i th species is given by

$$a_i^\dagger \Psi = z_i \Psi.$$

This takes a pure state $z^n = z_1^{n_1} \cdots z_i^{n_i} \cdots z_k^{n_k}$ to the pure state $z_1^{n_1} \cdots z_i^{n_i+1} \cdots z_k^{n_k}$ with one additional instance of the i th species. The corresponding **annihilation operator** is given by formal differentiation:

$$a_i \Psi = \frac{\partial}{\partial z_i} \Psi.$$

Given a pure state z^n , this represents moving to the state with one fewer instance of the i th species, albeit with a scaling coefficient n_i . This may be interpreted combinatorially, representing the fact that there are n_i ways to annihilate one of the n_i instances of the i th species present. This is appropriate as in this setting the law of mass action states that the rate of a transition is proportional to the number of distinct subsets of the present species that can form an input to the transition.

We now have the tools required for our definition of the master equation:

Definition 6. *The master equation for a stochastic Petri net (S, T, i, o, r) is*

$$\frac{d}{dt} \Psi(t) = H \Psi(t),$$

where the **Hamiltonian** H is given by

$$H = \sum_{\tau \in T} r(\tau) \left(a^{\dagger t(\tau)} - a^{\dagger s(\tau)} \right) a^{s(\tau)}.$$

Here again we use multi-index notation to define, for any $n \in \mathbb{N}^k$,

$$a^n = a_1^{n_1} \cdots a_k^{n_k}$$

and

$$a^{\dagger n} = a_1^{\dagger n_1} \cdots a_k^{\dagger n_k}.$$

For each transition τ , the first term $a^{\dagger t(\tau)} a^{s(\tau)}$ of the Hamiltonian describes how $s_i(\tau)$ things of the i th species get annihilated, and $t_i(\tau)$ things of the i th species get created. The second term $-a^{\dagger s(\tau)} a^{s(\tau)}$ is a bit harder to understand, but it describes how the probability that nothing happens—that we remain in the same pure state—decreases as time passes. This term must take precisely the form it does to ensure conservation of total probability. For a more detailed derivation of the Hamiltonian H , see the companion paper [4].

4 The Anderson–Craciun–Kurtz Theorem

From a certain class of equilibrium solutions of the rate equation, Anderson, Craciun, and Kurtz have proved that we may obtain equilibrium solutions of the master equation [1]. We now translate their

proof into the language of annihilation and creation operators, emphasizing the analogies between our Petri net systems and ideas in quantum mechanics. In particular, their equilibrium solution of the master equation is what people call a ‘coherent state’ in quantum mechanics.

To construct an equilibrium solution of the master equation from one for the rate equation, we require a ‘complex balanced’ solution. Here the term ‘complex’ again refers to a collection of instances of the given species, and a complex balanced solution is a solution in which not only the net rate of production of each species is zero, but furthermore the net rate of production of each possible *collection* of species is zero. For our Petri net, complexes are elements of \mathbb{N}^k , and the complexes of particular interest are the input complex $s(\tau)$ and the output complex $t(\tau)$ of each transition τ .

Definition 7. We say a classical state $c \in [0, \infty)^k$ is **complex balanced** if for all complexes $\kappa \in \mathbb{N}^k$ we have

$$\sum_{\{\tau:s(\tau)=\kappa\}} r(\tau)c^{s(\tau)} = \sum_{\{\tau:t(\tau)=\kappa\}} r(\tau)c^{s(\tau)}.$$

The left hand side of the above equation, which sums over the transitions in which the input complex is κ , gives the rate of consumption of the complex κ . The right hand side, which sums over the transitions in which the output complex is κ , gives the rate of production of κ . Thus the above equation requires that the net rate of production of the complex κ is zero when the number of things of each species is given by the vector c .

Any complex balanced classical state gives an equilibrium solution of the rate equation. Indeed, if $c \in [0, \infty)^k$ is a complex balanced classical state, then if $x(t) = c$ for all t we have

$$\frac{d}{dt}x(t) = \sum_{\tau \in T} r(\tau)(t(\tau) - s(\tau))c^{s(\tau)} = \sum_{\kappa \in \mathbb{N}^k} \kappa \left(\sum_{\{\tau:t(\tau)=\kappa\}} r(\tau)c^{s(\tau)} - \sum_{\{\tau:s(\tau)=\kappa\}} r(\tau)c^{s(\tau)} \right) = 0,$$

and so $x(t) = c$ is an equilibrium solution. In general, not every equilibrium solution of the rate equation is complex balanced. However, the ‘deficiency zero theorem’ [8, 12] says this holds for a large class of stochastic Petri nets.

The Anderson–Craciun–Kurtz theorem says that any complex balanced classical state also gives rise to an equilibrium solution of the master equation. Such solutions have a special form: they are ‘coherent states’. For any $c \in [0, \infty)^k$, we define the **coherent state** with expected value c to be the mixed state

$$\Psi_c = \frac{e^{c \cdot z}}{e^c}$$

where $c \cdot z$ is the dot product of the vectors c and z , and we set $e^c = e^{c_1 + \dots + c_n}$. Equivalently,

$$\Psi_c = \frac{1}{e^c} \sum_{n \in \mathbb{N}^k} \frac{c^n}{n!} z^n,$$

where c^n and z^n are defined as products in our usual way, and $n! = n_1! \dots n_k!$. The name ‘coherent state’ comes from quantum mechanics [15], in which we think of the coherent state Ψ_c as the quantum state that best approximates the classical state c . In the state Ψ_c , the probability of having n_i things of the i th species is equal to

$$e^{-c_i} \frac{c_i^{n_i}}{n_i!}.$$

This is precisely the definition of a Poisson distribution with mean equal to c_i . The state Ψ_c is thus a product of independent Poisson distributions.

It is remarkable that such a simple state can give an equilibrium solution of the master equation, even for very complicated stochastic Petri nets. But it is nonetheless true when c is complex balanced:

Theorem 1 (Anderson–Craciun–Kurtz). *Suppose $c \in [0, \infty)^k$ is a complex balanced classical state of a stochastic Petri net, and suppose that H is the Hamiltonian for the master equation of this stochastic Petri net. Then $H\Psi_c = 0$.*

Proof. Since Ψ_c is a constant multiple of $e^{c \cdot z}$, it suffices to show $He^{c \cdot z} = 0$. Recall that

$$H = \sum_{\tau \in T} r(\tau) \left(a^{\dagger t(\tau)} - a^{\dagger s(\tau)} \right) a^{s(\tau)}.$$

As the annihilation operator a_i is given by differentiation with respect to z_i , while the creation operator a_i^\dagger is just multiplying by z_i , we have

$$a^{s(\tau)} e^{c \cdot z} = c^{s(\tau)} e^{c \cdot z}, \quad a^{\dagger s(\tau)} e^{c \cdot z} = z^{s(\tau)} e^{c \cdot z},$$

and thus

$$He^{c \cdot z} = \sum_{\tau \in T} r(\tau) c^{s(\tau)} \left(z^{t(\tau)} - z^{s(\tau)} \right) e^{c \cdot z} = \sum_{i \in \mathbb{N}^k} \sum_{\tau \in T} r(\tau) c^{s(\tau)} \left(z^{t(\tau)} \frac{c^i}{i!} z^i - z^{s(\tau)} \frac{c^i}{i!} z^i \right),$$

where the second equality is given by expanding $e^{c \cdot z}$. If we then define negative powers to be zero and reindex, we may write

$$He^{c \cdot z} = \sum_{i \in \mathbb{N}^k} \sum_{\tau \in T} r(\tau) c^{s(\tau)} \left(\frac{c^{i-t(\tau)}}{(i-t(\tau))!} z^i - \frac{c^{i-s(\tau)}}{(i-s(\tau))!} z^i \right).$$

Hence, to show $He^{c \cdot z} = 0$, it is enough to show

$$\sum_{i \in \mathbb{N}^k} \sum_{\tau \in T} r(\tau) c^{s(\tau)} \frac{c^{i-t(\tau)}}{(i-t(\tau))!} z^i = \sum_{i \in \mathbb{N}^k} \sum_{\tau \in T} r(\tau) c^{s(\tau)} \frac{c^{i-s(\tau)}}{(i-s(\tau))!} z^i.$$

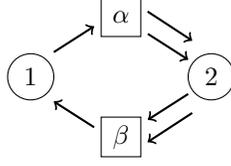
We do this by splitting the sum over the transitions T according to output and then input complexes, making use of the complex balanced condition in the equality marked (*):

$$\begin{aligned} & \sum_{i \in \mathbb{N}^k} \sum_{\tau \in T} r(\tau) c^{s(\tau)} \frac{c^{i-t(\tau)}}{(i-t(\tau))!} z^i \\ &= \sum_{i \in \mathbb{N}^k} \sum_{\kappa \in \mathbb{N}^k} \sum_{\{\tau: t(\tau)=\kappa\}} r(\tau) c^{s(\tau)} \frac{c^{i-t(\tau)}}{(i-t(\tau))!} z^i \\ &= \sum_{i \in \mathbb{N}^k} \sum_{\kappa \in \mathbb{N}^k} \frac{c^{i-\kappa}}{(i-\kappa)!} z^i \sum_{\{\tau: t(\tau)=\kappa\}} r(\tau) c^{s(\tau)} \\ &= \sum_{i \in \mathbb{N}^k} \sum_{\kappa \in \mathbb{N}^k} \frac{c^{i-\kappa}}{(i-\kappa)!} z^i \sum_{\{\tau: s(\tau)=\kappa\}} r(\tau) c^{s(\tau)} \tag{*} \\ &= \sum_{i \in \mathbb{N}^k} \sum_{\kappa \in \mathbb{N}^k} \sum_{\{\tau: s(\tau)=\kappa\}} r(\tau) c^{s(\tau)} \frac{c^{i-s(\tau)}}{(i-s(\tau))!} z^i \\ &= \sum_{i \in \mathbb{N}^k} \sum_{\tau \in T} r(\tau) c^{s(\tau)} \frac{c^{i-s(\tau)}}{(i-s(\tau))!} z^i. \end{aligned}$$

This proves the theorem. □

5 Example

Let us give a simple example of an equilibrium solution of a master equation derived from a complex balanced equilibrium solution of the rate equation. Consider the following stochastic Petri net with two species:



This represents a system where a single molecule of a diatomic gas splits into two individual atoms with rate constant α , while two atoms combine to form a molecule with rate constant β . The rate equation is:

$$\begin{aligned}\frac{dx_1}{dt} &= -\alpha x_1 + \beta x_2^2 \\ \frac{dx_2}{dt} &= 2\alpha x_1 - 2\beta x_2^2\end{aligned}$$

where x_1 and x_2 are the concentrations of species 1 and 2, respectively. Equilibrium occurs precisely when $\alpha x_1 = \beta x_2^2$.

The deficiency zero theorem implies that any equilibrium solution of the rate equation for this stochastic Petri net is complex balanced [8, 12]. Thus, we can apply the Anderson–Craciun–Kurtz theorem to obtain equilibrium solutions of the master equation. The master equation takes the form

$$\frac{d}{dt}\Psi(t) = H\Psi(t)$$

with

$$H = \alpha(a_2^\dagger a_2^\dagger - a_1^\dagger)a_1 + \beta(a_1^\dagger - a_2^\dagger a_2^\dagger)a_2 a_2 = (z_2^2 - z_1) \left(\alpha \frac{\partial}{\partial z_1} - \beta \frac{\partial^2}{\partial z_2^2} \right).$$

Given the complexity of this Hamiltonian, it might seem difficult to find exact solutions of $H\Psi = 0$. But by the Anderson–Craciun–Kurtz theorem, whenever c gives a complex balanced equilibrium for the rate equation, meaning $\alpha c_1 = \beta c_2^2$, the following coherent state is a solution:

$$\Psi_c = \frac{e^{c_1 z_1 + c_2 z_2}}{e^{c_1 + c_2}}.$$

To see this, we need only note that

$$(z_2^2 - z_1) \left(\alpha \frac{\partial}{\partial z_1} - \beta \frac{\partial^2}{\partial z_2^2} \right) e^{c_1 z_1 + c_2 z_2} = (z_2^2 - z_1)(\alpha c_1 - \beta c_2^2) e^{c_1 z_1 + c_2 z_2}.$$

This vanishes precisely when $\alpha c_1 = \beta c_2^2$.

Note that

$$\Psi_c = \frac{1}{e^{c_1} e^{c_2}} \sum_{(n_1, n_2) \in \mathbb{N}^2} \frac{c_1^{n_1} c_2^{n_2}}{n_1! n_2!} z_1^{n_1} z_2^{n_2},$$

so

$$\psi_{n_1, n_2} = \frac{1}{e^{c_1} n_1!} \cdot \frac{1}{e^{c_2} n_2!}.$$

This is a product of two independent Poisson distributions. It may seem disturbing that in a reaction where one species turns into another there are equilibrium solutions where the numbers of things of

each kind are independent random variables. Intuitively, it might seem that having more things of species 1 would force there to be fewer of species 2.

In fact this intuition is misleading. However, there are other equilibrium solutions of the master equation that are not products of independent probability distributions. To see this, suppose we take any of our equilibrium solutions Ψ_c and construct a state $\Psi^{(n)}$ by setting the probability $\psi_{n_1, n_2}^{(n)}$ equal to $\lambda \psi_{n_1, n_2}$ when $2n_1 + n_2 = n$ and zero otherwise, where λ is the constant required for $\Psi^{(n)}$ to be normalized.

It is readily checked that $\Psi^{(n)}$ is also an equilibrium solution for our reversible chemical system. The key observation is that this particular stochastic Petri net has a ‘conserved quantity’: the total number of atoms, $2n_1 + n_2$. A pure state (n_1, n_2) may only transition to another pure state (n'_1, n'_2) if $2n_1 + n_2 = 2n'_1 + n'_2$. This allows us to take any equilibrium solution of the master equation and, in the language of quantum mechanics, ‘project down to the subspace’ where this conserved quantity takes a definite value, to obtain a new equilibrium solution. In the language of probability theory, this is ‘conditioning on’ the conserved quantity taking a definite value.

Thanks to the stochastic version of Noether’s theorem, conserved quantities correspond to symmetries of the Hamiltonian [6]. In the example at hand, the conserved quantity is

$$O = 2N_1 + N_2,$$

where N_i is the **number operator** for the i th species:

$$N_i = a_i^\dagger a_i.$$

The states $z^n = z_1^{n_1} z_2^{n_2}$ are a basis of eigenvectors of these number operators:

$$N_i z^n = n_i z^n,$$

so they are also a basis of eigenvectors of O :

$$O z^n = (2n_1 + n_2) z^n.$$

By the argument already given, time evolution according to the Hamiltonian H preserves each eigenspace of O , so we have

$$[\exp(tH), O] = 0$$

for all $t \geq 0$, where the commutator $[A, B]$ of operators is defined to be $AB - BA$. This says that O is a conserved quantity.

On the other hand, we also have

$$[H, \exp(sO)] = 0$$

for all $s \in \mathbb{R}$. This says that O generates a 1-parameter group of symmetries of the Hamiltonian H . This symmetry can be seen to have the following effect on coherent states:

$$\exp(sO) \Psi_c = \frac{e^{c'}}{e^c} \Psi_{c'}$$

where

$$(c'_1, c'_2) = (e^{2s} c_1, e^s c_2).$$

Note that if c is an equilibrium solution of the rate equation, so is c' .

Modulo nuances of analysis involving unbounded operators, both $[\exp(tH), O] = 0$ and $[H, \exp(sO)] = 0$ are equivalent to the more easily checked equation

$$[H, O] = 0,$$

and both are also equivalent to

$$[\exp(tH), \exp(sO)] = 0$$

for all $s, t \in \mathbb{R}$. This last equation says that applying the symmetry $\exp(sO)$ to a state Ψ and then evolving it for a time t according to the master equation gives the same result as first evolving Ψ for a time t according to the master equation and then applying the symmetry.

This example illustrates some general phenomena. In chemical reactions, the total number of atoms of each element is conserved, so there will always be some conserved quantities O_1, \dots, O_n that are linear combinations of number operators. Such conserved quantities always commute, since number operators commute. Given a complex balanced classical state c we can obtain an equilibrium solution Ψ_c of the master equation using the Anderson–Craciun–Kurtz theorem. We can then obtain other equilibrium solutions of the master equation in two ways:

- We can project down Ψ_c to any subspace where the observables O_i take definite values:

$$\{\Psi : O_i \Psi = \lambda_i \Psi\}$$

for some nonnegative numbers λ_i .

- We can apply symmetries of the form $\exp(s_1 O_1 + \dots + s_n O_n)$ to Ψ_c . As well known in quantum mechanics, the result will be, up to normalization, another coherent state:

$$\exp(s_1 O_1 + \dots + s_n O_n) \Psi_c = \frac{e^{c'}}{e^c} \Psi_{c'}$$

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