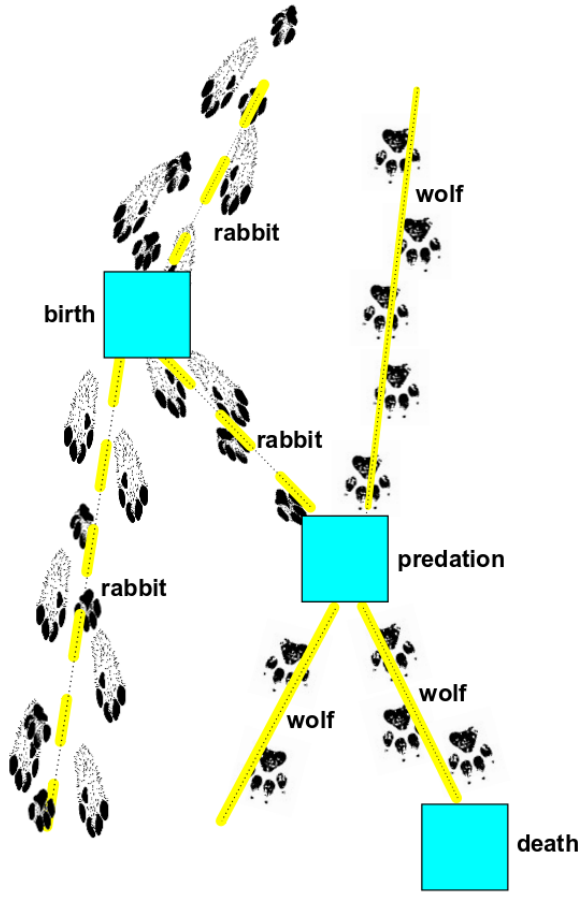
Probabilities versus Amplitudes



John Baez, Jacob Biamonte, Brendan Fong
Mathematical Trends in Reaction Network Theory
1 July 2015

Chemistry is fundamentally quantum-mechanical. But the master equation describes reactions using classical probability theory.

We usually compute a probability $p \in [0,1]$ from an amplitude $\psi \in \mathbb{C}$ as follows:

$$p = |\psi|^2.$$

We'd need to use this idea to derive the master equation as an approximation to quantum chemistry.

That's not what I'm going to do!

Instead, I'll show how the master equation fits into a strange but thorough-going *analogy* between probabilities and amplitudes:

$$p \sim \psi$$

Suppose we have a system with n possibilities:

$$X = \{1, \ldots, n\}$$

In quantum theory we consider **quantum states**:

$$\psi \colon X \to \mathbb{C}$$

with

$$\sum_{i \in X} |\psi_i|^2 = 1$$

In probability theory we consider **stochastic states**:

$$\psi \colon X \to \mathbb{R}$$

with

$$\sum_{i \in X} \psi_i = 1 \quad \text{and} \quad \psi_i \geq 0$$

A linear operator $U\colon \mathbb{C}^n \to \mathbb{C}^n$ that maps quantum states to quantum states is called **unitary**.

A linear operator $U\colon \mathbb{R}^n \to \mathbb{R}^n$ that maps stochastic states to stochastic states is called **stochastic**.

Concretely, U is unitary iff

$$\sum_i |U_{ij}|^2 = 1$$

and stochastic iff

$$\sum_i U_{ij} = 1 \text{ and } U_{ij} \geq 0$$

A linear operator $H\colon \mathbb{C}^n \to \mathbb{C}^n$ for which $\exp(-itH)$ is unitary for all $t \in \mathbb{R}$ is called **self-adjoint**.

A linear operator $H\colon \mathbb{R}^n \to \mathbb{R}^n$ for which $\exp(tH)$ is stochastic for all $t \in [0, \infty)$ is called **infinitesimal stochastic**.

Concretely, H is self-adjoint iff

$$H_{ji} = \overline{H_{ij}}$$

and infinitesimal stochastic iff

$$\sum_i H_{ij} = 0 \text{ and } H_{ij} \geq 0 \text{ if } i \neq j$$

If H is self-adjoint, we can describe time evolution of quantum states using **Schrödinger's equation**:

$$\frac{d}{dt}\psi(t) = -iH\psi(t)$$

If H is infinitesimal stochastic, we can describe time evolution of stochastic states using the **master equation**:

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

In both cases, let's call H the **Hamiltonian**.

Unitary operators have unitary inverses; stochastic operators rarely have stochastic inverses! So, we only evolve forwards in time in stochastic mechanics.

Suppose we have a finite set S of species. An element $\kappa \in \mathbb{N}^S$ is a **complex**: it says how many items of each species we have.

In quantum mechanics, let $\psi_\kappa \in \mathbb{C}$ be the amplitude that we have exactly κ_i items of the ith species for each $i \in S$. We thus have a function $\psi \colon \mathbb{N}^S \to \mathbb{C}$, which is a **quantum state** if

$$\sum_{\kappa \in \mathbb{N}^S} |\psi_\kappa|^2 = 1$$

We define **Fock space** to consist of functions $\psi \colon \mathbb{N}^S \to \mathbb{C}$ with

$$\sum_{\kappa \in \mathbb{N}^S} |\psi_\kappa|^2 < \infty$$

We describe time evolution by $\frac{d}{dt}\psi(t) = -iH\psi(t)$.

In stochastic mechanics, let ψ_κ be the *probability* that we have exactly κ_i items of the ith species for each $i \in S$.

Thus we have a function $\psi\colon \mathbb{N}^S \to \mathbb{R}$, which is a **stochastic state** if

$$\sum_{\kappa \in \mathbb{N}^S} \psi_\kappa = 1 \quad \text{and} \quad \psi_\kappa \geq 0$$

We define the **stochastic Fock space** to consist of functions $\psi\colon \mathbb{N}^S \to \mathbb{R}$ with

$$\sum_{\kappa \in \mathbb{N}^S} |\psi_\kappa| < \infty$$

We describe time evolution by $\dfrac{d}{dt}\psi(t) = H\psi(t)$.

In quantum mechanics, we often build the Hamiltonian H on Fock space from 'annihilation' and 'creation' operators. We can do the same in stochastic mechanics!

Let's see how to define H in this example from biology:

$$\text{fission: amoeba} \to \text{amoeba} + \text{amoeba}$$
$$\text{competition: amoeba} + \text{amoeba} \to \text{amoeba}$$

Suppose ψ_n is the probability of having n amoebas. We can summarize this information in a power series:

$$\Psi(z) = \sum_{n=0}^{\infty} \psi_n z^n$$

The **creation operator** $a^\dagger$ creates an amoeba:

$$a^\dagger \Psi = z\Psi$$

The **annihilation operator** a destroys one:

$$a\Psi = \frac{d}{dz}\Psi$$

Note that $az^n = nz^{n-1}$. The idea: there are n amoebas to choose from!

The **commutator** of operators A, B is defined by

$$[A, B] = AB - BA$$

The annihilation and creation operators obey

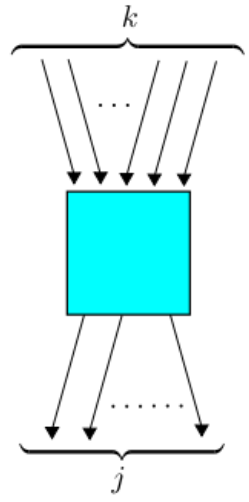
$$[a, a^\dagger] = 1$$

This noncommutativity is fundamental to quantum mechanics. Does it make sense for classical objects if we use probabilities instead of amplitudes?

Yes!

Let's see how it works.

We would like a Hamiltonian for a process that destroys k amoebas and creates j of them:



The obvious guess is $a^{\dagger j} a^k$. But this is not infinitesimal stochastic! The right answer has a 'correction term':

$$a^{\dagger j} a^k - a^{\dagger k} a^k$$

For example, $H = a^\dagger - 1$ describes the random 'creation' of amoebas.

Then the master equation has this solution:

$$\Psi(t) = e^{t(z-1)}\Psi(0)$$

Check:

$$\begin{aligned}
\frac{d}{dt}\Psi(t) &= \frac{d}{dt}e^{t(z-1)}\Psi(0) \\
&= (z-1)e^{t(z-1)}\Psi(0) \\
&= (a^\dagger - 1)\Psi(t) \\
&= H\Psi(t)
\end{aligned}$$

Does this solution do what we want?

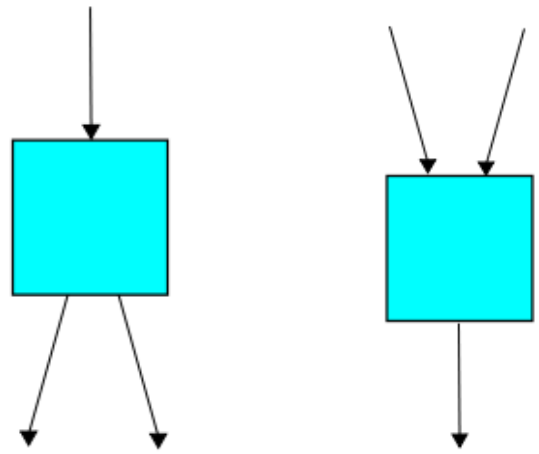
$$\Psi(t) = e^{t(z-1)}\Psi(0)$$

If we start with the 'vacuum state' $\Psi(0) = 1$, where there are no amoebas, at time t we have

$$\Psi(t) = e^{t(z-1)} = e^{-t}\sum_n \frac{t^n}{n!}z^n$$

so the probability of having n amoebas is $e^{-t}\frac{t^n}{n!}$. This is just what we expect: a Poisson process.

The reaction network we care about has two reactions: *fission* and *competition*:



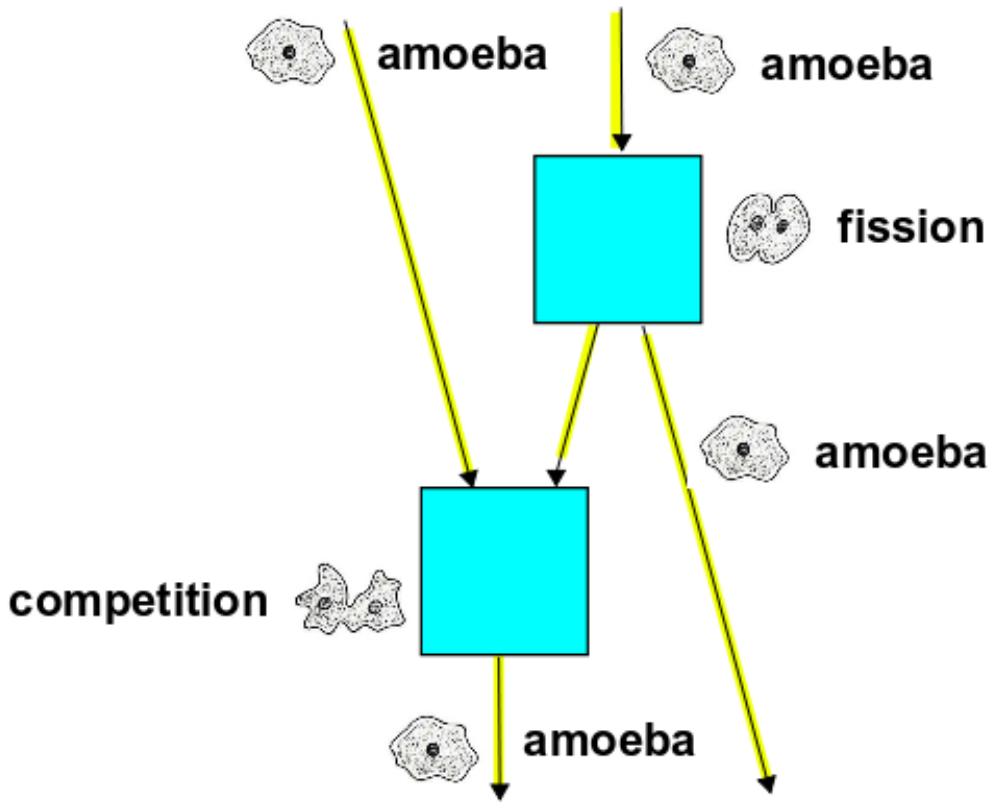
So, if these have rate constants α and β, we get

$$H = \alpha(a^{\dagger 2}a - a^{\dagger}a) \quad + \quad \beta(a^{\dagger}a^2 - a^{\dagger 2}a^2)$$

We can express the time evolution operator

$$\exp(tH) = 1 + tH + \frac{t^2}{2!}H^2 + \cdots$$

as a sum over Feynman diagrams:



All this works quite generally. Suppose we have k different species. Write

$$S = \{1, \ldots, k\}$$

A typical element of the stochastic Fock space can be written as

$$\Psi = \sum_{\kappa \in \mathbb{N}^k} \psi_\kappa \; z^{\kappa_1} \cdots z^{\kappa_k}$$

where $\psi_\kappa \in \mathbb{R}$ and

$$\sum_\kappa |\psi_\kappa| < \infty$$

We have annihilation and creation operators on the stochastic Fock space:

$$a_i \Psi = \frac{\partial \Psi}{\partial z_i} \qquad\qquad a_i^\dagger \Psi = z_i \Psi$$

More generally, for any complex κ we have operators that annihilate or create that whole complex:

$$a^\kappa = a_1^{\kappa_1} \cdots a_k^{\kappa_k} \qquad\qquad a^{\dagger \kappa} = a_1^{\dagger \kappa_1} \cdots a_k^{\dagger \kappa_k}$$

Suppose we have a set T of reactions where the reaction $\tau \in T$ turns the complex $s(\tau)$ into the complex $t(\tau)$. Suppose the reaction τ has rate constant $r(\tau)$. Then our Hamiltonian is a sum over reactions:

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

You can check that

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

gives the chemical master equation you know and love!

In quantum mechanics, the basic structure on states is the inner product, which for $\mathbb{C}^n$ is

$$\langle \psi, \phi \rangle = \sum_i \overline{\psi}_i \phi_i$$

In stochastic mechanics, the corresponding structure on $\mathbb{R}^n$ is

$$\langle \psi \rangle = \sum_i \psi_i$$

In quantum mechanics, the **expected value** of a linear operator $O\colon \mathbb{C}^n \to \mathbb{C}^n$ in the quantum state ψ is

$$\langle \psi, O\psi \rangle$$

In stochastic mechanics, the **expected value** of $O\colon \mathbb{R}^n \to \mathbb{R}^n$ in the stochastic state ψ is

$$\langle O\psi \rangle$$

This is most familiar when O is diagonal: if $O_{ij} = O_i \delta_{ij}$ then

$$\langle O\psi \rangle = \sum_i O_i \psi_i$$

In either quantum or stochastic mechanics we can define **number operators** on Fock space:

$$N_i = {a_i}^\dagger a_i$$

The expected value of N_i in a state Ψ is the expected number of items of the ith species.

In the quantum case this means that

$$\langle \Psi, N_i \Psi \rangle = \sum_\kappa \kappa_i |\psi_i|^2$$

In the stochastic case,

$$\langle N_i \Psi \rangle = \sum_\kappa \kappa_i \psi_\kappa$$

In quantum mechanics, the expected value of any operator O changes as follows:

$$\frac{d}{dt}\langle\Psi(t), O\Psi(t)\rangle = -i\langle\Psi(t),\ [O,H]\Psi(t)\rangle$$

when $\Psi(t)$ obeys Schrödinger's equation.

In stochastic mechanics, it changes as follows:

$$\frac{d}{dt}\langle O\Psi(t)\rangle = \langle[O,H]\Psi(t)\rangle$$

when $\Psi(t)$ obeys the master equation.

Using the Hamiltonian we've seen for a chemical reaction network:

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

we can use everything I've said so far to prove

$$\frac{d}{dt} \langle N \Psi(t) \rangle = \sum_{\tau \in T} r(\tau) \left(s(\tau) - t(\tau) \right) \left\langle N^{\underline{s(\tau)}} \Psi(t) \right\rangle$$

where we define the **falling power** of a number operator by

$$N_i^{\underline{p}} = N_i (N_i - 1) \cdots (N_i - p + 1)$$

or for any complex κ,

$$N^{\underline{\kappa}} = N_1^{\underline{\kappa_1}} \cdots N_k^{\underline{\kappa_k}}$$

In a suitable large-number limit,

$$\frac{d}{dt}\langle N\Psi(t)\rangle = \sum_{\tau\in T} r(\tau)\,(s(\tau)-t(\tau))\,\left\langle N^{\underline{s(\tau)}}\,\Psi(t)\right\rangle$$

reduces to the *rate equation* for our chemical reaction network.

This is not really new. However, what's nice is that this 'large-number limit' is precisely analogous to the *classical limit* of quantum mechanics: the limit where $\hbar \to 0$.

For details see:

- John Baez and Jacob Biamonte, *A Course on Quantum Techniques for Stochastic Mechanics*.
- John Baez and Arjun Jain, The large-number limit for reaction networks.