

# Field Theory Methods in Reaction-Diffusion Systems

Gregory Szep

*King's College London*

June 1, 2018

## 1 Dynamical Systems Approach

In this section we will set the scene for chemical reaction systems and their methods of analysis of steady state and network perspectives. Dynamical methods makes use of field flow, linear stability and bifurcation analysis.

### 1.1 Reaction Kinetics

Consider  $N$  particles of  $S$  species in a finite volume  $\Omega$ . These particles can undergo  $R$  possible reactions when they meet within the volume. Suppose the timescales of equilibration with respect to volume and temperature are much faster than that of species number equilibration. This means that non-reactive collisions occur more frequently than collisions that trigger any of the  $R$  reactions. This is the essence of the *well-mixed* approximation [1].

This suggests that at any time  $t$  we may ignore spatial inhomogeneities and pin down the state of the system by a vector of species populations  $s(t) \in \mathbb{N}^S$ . All possible reactions in the mixture are encoded into a stoichiometric matrix  $\mathbf{\Gamma} \in \mathbb{Z}^{S \times R}$  whos columns  $\mathbf{\Gamma}[r] \in \mathbb{Z}^S$  represent the population change vector for a given reaction  $r$ . Each reaction has a propensity  $\omega(r|s) \in [0, \infty)$  defined though transition probabilities for an infinitesimal time interval given population  $s$ ;

$$\omega(r|s)dt := \mathbb{P}(s + \mathbf{\Gamma}[r], t + dt | s, t) \quad (1.1)$$

Suppose  $\sigma[r]dt$  gives the probability that the reaction  $r$  will occur within the time interval  $dt$  independent of population  $s$ . The constant  $\sigma[r]$  could be in principle calculated from the microscopic physics of the reaction. In quantum mechanics this would involve calculating the wavefunction overlap or transition rates between initial and final configurations.

The propensity is proportional this rate, up to combinatoric multiplicity taking into account the species population  $s$ . A reaction  $r$  chooses  $g[i, r]$  particles for each reactant species  $i$  from the *well-mixed* solution containing  $s[i]$  particles. Thus the multiplicity is simply given by a binomial coefficient per species. This results in a propensity that is polynomial in the components  $s[i]$ , where the highest power term gives us the *order* of the reaction.

$$\omega(r|s) = \sigma[r] \prod_{i=1}^S \binom{s[i]}{g[i, r]} \quad (1.2)$$

For reactions involving distinguishable particle species, all components  $g[i, r] \in \{0, 1\}$  and simplifies the combinatoric term to a product of all reactant populations.

$$g[i, r] \in \{0, 1\} \quad \forall i, r \quad \implies \quad \omega(r|s) = \sigma[r] \prod_{i=1}^S s[i]^{g[i, r]} \quad (1.3)$$

### 1.1.1 Chemical Master Equation

By applying the laws of probability and taking the  $dt \rightarrow 0$  one can derive — see Appendix A for details — a time-evolution equation  $\mathbb{P}(s, t)$  involving the definition (1.1) which has become known as the Chemical Master Equation [1, 2]. Note here the complexity lies within the nonlinear state dependence in the propensity  $\omega(r|s)$ . Were it not for this, we could solve this equation using spectral methods.

$$\partial_t \mathbb{P}(s, t) = \sum_{r=1}^R \omega(r|s - \mathbf{\Gamma}[r]) \mathbb{P}(s - \mathbf{\Gamma}[r], t) - \omega(r|s) \mathbb{P}(s, t) \quad (1.4)$$

Multiplying the Chemical Master Equation (1.4) by  $s$  and summing over all  $s$  obtains a system of differential equations for the first moment  $\langle s \rangle$  in terms of vectorised propensity  $\omega(s|\mathbf{\Gamma}) \in [0, \infty)^R$  which couples to higher order moments, unfolding an infinite hierarchy.

$$\partial_t \langle s \rangle = \mathbf{\Gamma} \langle \omega(s|\mathbf{\Gamma}) \rangle \quad (1.5)$$

### 1.1.2 Reaction Equation

The mean field approximation factorises higher order moments, implying  $\langle f(s) \rangle = f(\langle s \rangle)$  for any nonlinear function  $f$ . This is equivalent to neglecting fluctuations in the  $N, \Omega \rightarrow \infty$  thermodynamic limit, and it is here where the mass-action assumption becomes manifest [2].

This closes the infinite hierarchy (1.5) yielding a nonlinear set of coupled ordinary differential equations for a continuous vector field  $\psi(t) \in [0, \infty)^S$ . These have come to be known as the Reaction Rate Equations, and are typical for modelling processes in systems biology.

$$\partial_t \psi = \Gamma \omega(\psi | \Gamma) \quad (1.6)$$

### 1.1.3 Bifurcation Analysis

In the mean field approximation (1.6) we may investigate the steady state  $\partial_t \psi = 0$ . This gives rise to a set of  $S$  polynomial equations in the components  $\psi[s] \in [0, \infty)$  of steady state  $\psi^*$ . These define  $S - 1$  dimensional nullcline hypersurfaces embedded in  $S$  dimensional state space.

$$\sum_{r=1}^R \Gamma[s', r] \sigma[r] \prod_{s=1}^S \left( \frac{\psi[s]}{g[s, r]} \right) \Big|_{\psi=\psi^*} = 0 \quad \forall s' = 1, 2, \dots, S \quad (1.7)$$

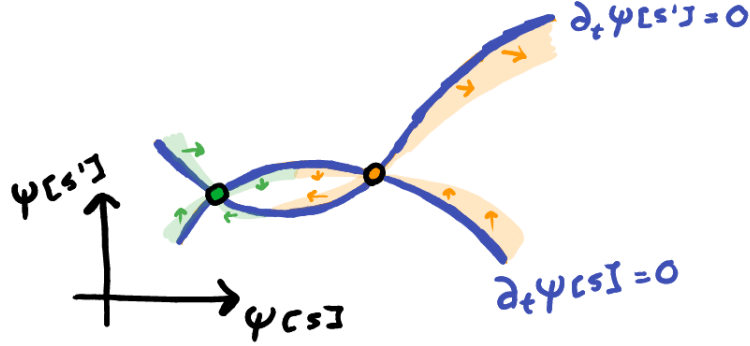


Figure 1: Schematic of two nullclines with their orthogonal local field flows intersecting at **stable** and **unstable** fixed points  $\psi^*$

Nullclines determine local direction of evolution of the system. On a given nullcline  $\partial_t \psi[s] = 0$  the flow of the field must be orthogonal to the direction of  $\psi[s]$ . At intersections between two nullclines, the flow must be orthogonal to the plane defined by two axes. At the intersections between all nullclines we may find the fixed points  $\psi^*$  as shown in Figure 1.

Classification of fixed points  $\psi^*$  is done by linearising the equation of motion (1.6) with respect to field perturbation  $\varepsilon(t)$  in their vicinity and determining the eigenvalues of the resultant  $S \times S$  Jacobian  $\mathbf{J}(\psi)$  evaluated at each fixed point  $\psi^*$ .

$$\varepsilon(t) \sim e^{\mathbf{J}(\psi)|_{\psi=\psi^*} t} \quad (1.8)$$

$$\text{where } J[i, j] = \sum_{r=1}^R \sigma[r] \left( H(\psi[i]) - H(\psi[i] - g[i, r]) \right) \Gamma[j, r] \prod_{s=1}^S \left( \frac{\psi[s]}{g[s, r]} \right) \quad (1.9)$$

$$H(x) = \int_0^1 \frac{1-t^x}{1-t} dt \quad \text{are generalised Harmonic Numbers} \quad (1.10)$$

For reactions involving one or two distinguishable particles as in (1.3) the nullclines become hyperplanes and the Jacobian simplifies. We can see that both the reaction topology given by stoichiometric coefficients  $\Gamma[i, j]$  and the reaction rates  $\sigma[r]$  contribute to rotating and shifting the hyperplanes and determining the location and stability of their intersections.

$$J[i, j] = \sum_{r=1}^R \sigma[r] |\Gamma[i, r]| \Gamma[j, r] \prod_{s \neq i} \psi[s]^{g[i, r]} \quad g[i, r] \in \{0, 1\} \quad \forall i, r \quad (1.11)$$

The sign of eigenvalues  $\lambda$  of Jacobian  $\mathbf{J}$  determine whether a fixed point is stable  $\lambda < 0$  or unstable  $\lambda > 0$ . As an illustrative example we can characterise fixed points given an arbitrary two dimensional Jacobian. Figure 2 reveals the regions of stability and phase space flows.

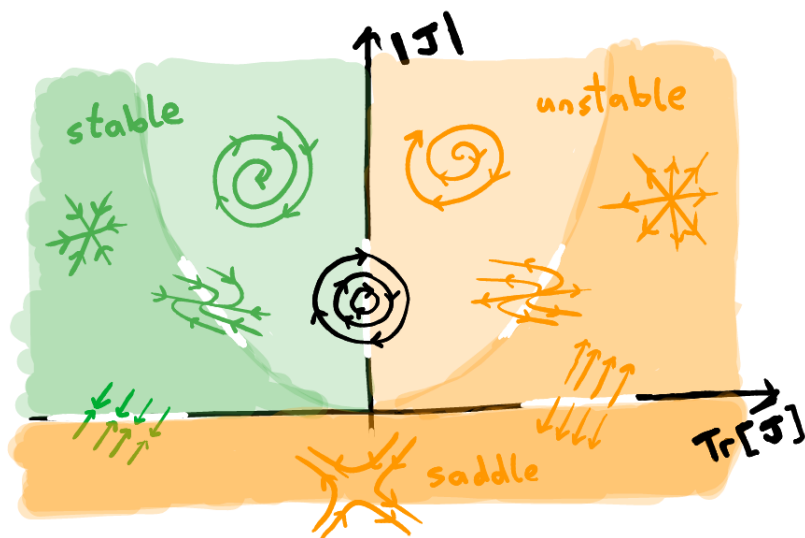


Figure 2: Classification of **stable** and **unstable** fixed points for a general two dimensional Jacobian in terms of trace  $\text{Tr}[\mathbf{J}]$  and determinant  $|\mathbf{J}|$

Varying the continuous parameters  $\sigma[r]$  moves the nullclines and may result in the creation or annihilation of fixed points of different classes. While an individual fixed point may change location and local phase space flow, it cannot change class without involving another fixed point.

These are called bifurcations and also fall into various categories. Figure 3 illustrates some of the possible one parameter supercritical bifurcations; subcritical cases are obtained by permuting stabilities of fixed points. Note the hysteresis loop in the saddle-node bifurcation.

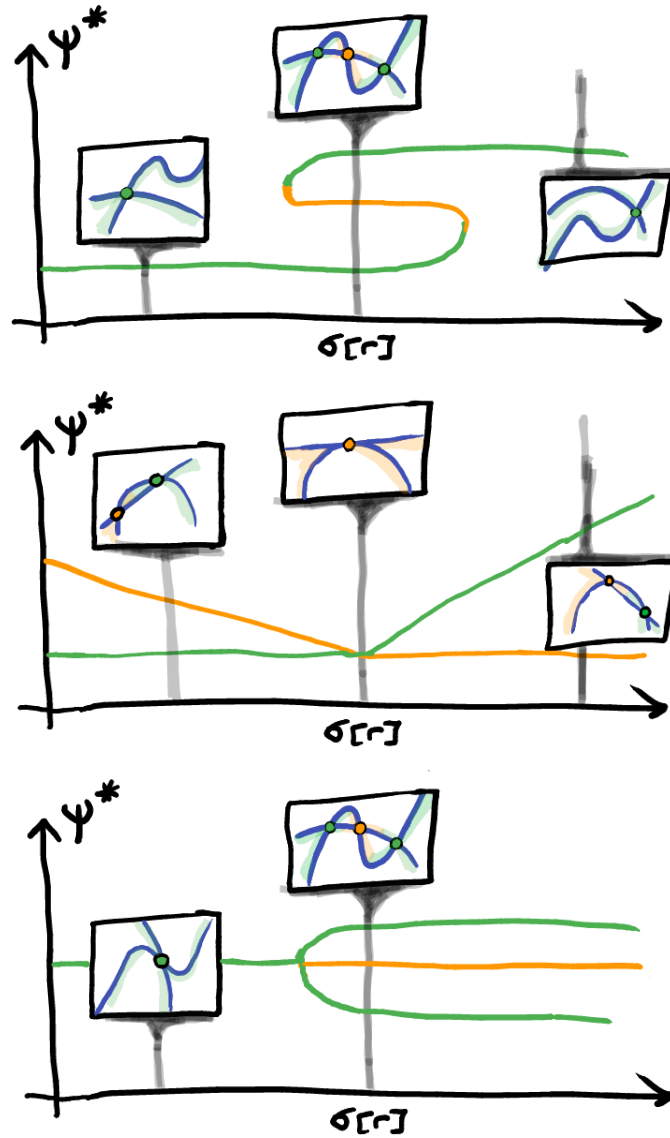


Figure 3: Saddle-node, Transcritical and Pitchfork bifurcation diagram showing **stable** and **unstable** fixed points  $\psi^*$  as a function of parameter  $\sigma[r]$ . Insets show nullcline intersections.

Another category of bifurcations involves limit cycles, which emerge from fixed points where the linearised Jacobian eigenvalues have no real part. Limit cycles have circulating field flow as shown in Figure 2 along the  $\text{Tr}[\mathbf{J}] = 0$ ,  $|\mathbf{J}| > 0$  axis.

Note how oscillations emerge at small amplitudes in the Hopf bifurcation, whereas the large amplitude oscillations may instantly emerge in an infinite-period or cyclic-fold bifurcation. In Figure 4 the shaded regions represent the peaks and troughs of the oscillations.

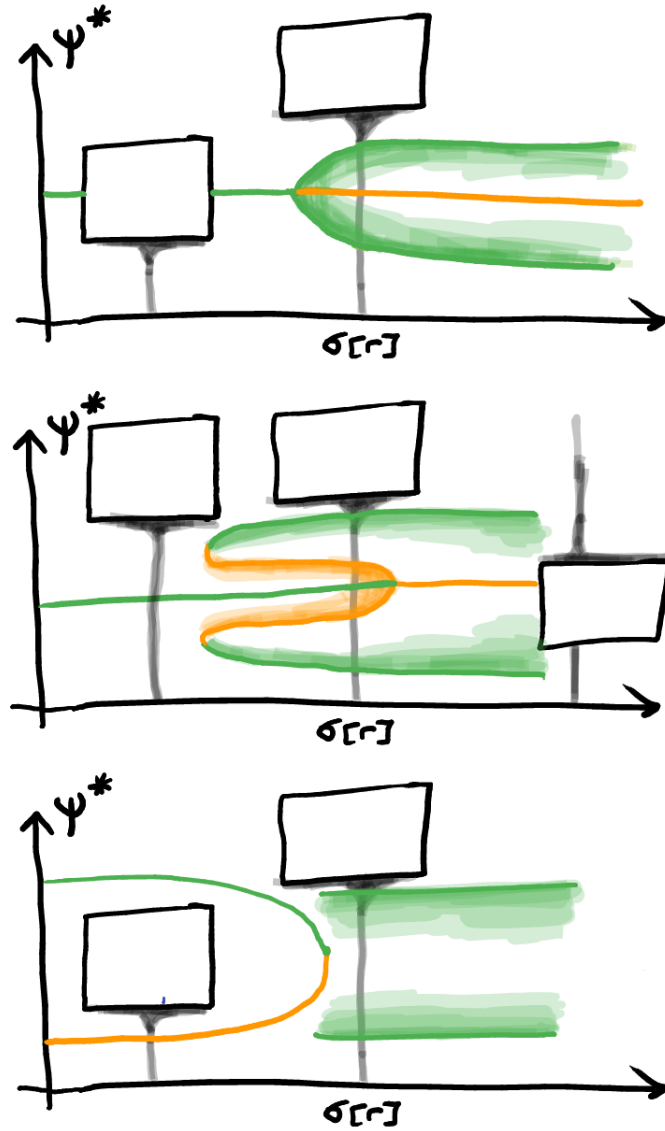


Figure 4: Hopf, Cyclic-fold and Infinite-Period bifurcation diagram showing **stable** and **unstable** fixed points and limit cycles as a function of parameter  $\sigma[r]$ . Insets show nullclines [tbc]

#### **1.1.4 Attractor Geometry and Universality**

In this section we would explore the geometrisation of phase space, lyapunov exponents and universality. Perhaps a discussion on phase transitions and the relation to Landau-Ginzberg approaches is required. Maybe also periodic orbit theory? Depends how useful it is.

#### **1.1.5 Reaction-Diffusion**

Here we first introduce diffusion macroscopically by simply adding the laplacian to mean field equation (1.6). We introduce the turning bifurcation and show how linear stability analysis is insufficient to capture pattern formation and rich inhomogenous steady states. A promising approach may be geometrisation of the moving local equilibria [3].

## 2 Field Theory Approach

Taking the mean-field thermodynamic limit gives rise to a set of coupled nonlinear ordinary differential equations, whose steady states and limit cycles can be investigated readily. Timescales and dynamical information beyond linear stability however are more difficult to extract. A field theory approach makes use of diagrammatic expansions and Green's Functions allowing for calculation of correlations and observables.

### 2.1 Doi Representation

#### 2.1.1 Reaction Term

The starting point for setting up the field theory is casting of the nonlinear equations of motion into a space in which the state evolves according to a linear equation with the complexity compressed into the operator [4].

Suppose we define orthonormal basis  $|s\rangle$  to represent  $s[i]$  particles for all species  $i = 1 \dots S$ . Discreteness suggests we should introduce field operators  $\hat{a}_i, \hat{a}_i^\dagger$  that remove/add one particle of species  $i$  from/to the state  $|s\rangle$ . Here  $\delta_{ij}$  is the delta and the indicator vector  $\mathbb{1}_i[j] := \delta_{ij}$ .

$$\hat{a}_i |s\rangle := s[i] |s - \mathbb{1}_i\rangle \quad \hat{a}_i^\dagger |s\rangle := |s + \mathbb{1}_i\rangle \quad (2.1)$$

It can be shown — see Appendix B — with such chosen normalisation these operators satisfy the usual bosonic commutation relations and define the number operator in the usual way.

$$\begin{aligned} \hat{a}_i^\dagger \hat{a}_i |s\rangle &= s[i] |s\rangle & [\hat{a}_i, \hat{a}_j^\dagger] &= \delta_{ij} \\ [\hat{a}_i, \hat{a}_j] &= [\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0 \end{aligned} \quad (2.2)$$

Moreover it becomes possible to have an operator representation of the propensity  $\hat{\omega}(r)$  and shifts independent of the state  $s$ .

$$\hat{\omega}(r) |s\rangle = \omega(r|s) |s\rangle \quad \hat{\omega}(r) := \lambda[r] \prod_{i=1}^S \hat{a}_i^{\dagger g[i,r]} \hat{a}_i^{g[i,r]} \quad \lambda[r] = \frac{\sigma[r]}{\prod_{i=1}^S g[i,r]!} \quad (2.3)$$

$$|s + n\rangle = \prod_{i=1}^S \hat{a}_i^{\dagger n[i]} |s\rangle \quad \text{where} \quad \hat{a}_i^{-\dagger} |s\rangle = |s - \mathbb{1}_i\rangle \quad (2.4)$$



Defining the time-dependent state  $|\Psi(t)\rangle$  as a linear combination of all possible states  $|s\rangle$  with coefficients  $\mathbb{P}(s, t)$  which evolve according to the Chemical Master Equation (1.4) allows us to write down a Schrödinger equation with Hamiltonian  $\hat{\mathcal{R}}$ . The equation can be obtained by using the operator representation of the propensity and shifting indices  $s$  in the sum.

$$\mathbb{I} \partial_t |\Psi(t)\rangle = \hat{\mathcal{R}} |\Psi(t)\rangle \quad \text{where} \quad |\Psi(t)\rangle := \sum_{s \in \mathbb{N}^S} \mathbb{P}(s, t) |s\rangle \quad (2.5)$$

$$\hat{\mathcal{R}} = \mathbb{I} \sum_{r=1}^R \lambda[r] \left( \prod_{i=1}^S \hat{a}_i^{\dagger \Gamma[i, r]} - \hat{\mathbb{1}} \right) \prod_{j=1}^S \hat{a}_j^{\dagger g[j, r]} \hat{a}_j^{g[j, r]} \quad (2.6)$$

Amazing! We are now ready to import methods from Quantum Mechanics from diagrammatic expansions through to non-equilibrium Green's Functions and Feynman path integrals. Let us pause and ponder this Hamiltonian: it is non-Hermitian and therefore leads to irreversible dynamics; the term involving  $g[i, r]$  is zero unless the state contains  $g[i, r]$  particles of species  $i$ , defining the *order* of reaction  $r$ ; if the right species are present the term involving  $\Gamma[i, r]$  is non-zero for  $\Gamma[i, r] \neq 0$  with the state change encoded by creation, and inverse-creation operators.

### 2.1.2 Diffusion Term

We consider diffusion on an  $M$ -dimensional lattice for a discrete state, continuous space-time process. For now let's consider a single species  $s \in \mathbb{N}$  and let  $\mathbb{P}(s_{\mathbf{x}} \dots s_{\mathbf{y}}, t)$  be the joint probability of finding  $s_{\mathbf{x}} \dots s_{\mathbf{y}}$  particles in locations  $\mathbf{x} \dots \mathbf{y} \in \mathbb{R}^M$  at time  $t$ . Particles at  $\mathbf{x}$  may jump to/from neighbourhood  $\partial \mathbf{x}$ .

$$\partial_t \mathbb{P}(s_{\mathbf{x}} \dots s_{\mathbf{y}}, t) = D \int_{\mathbb{R}^M} \int_{\partial \mathbf{x}} (s_{\mathbf{y}} + 1) \mathbb{P}(s_{\mathbf{x}} - 1 \dots s_{\mathbf{y}} + 1, t) - s_{\mathbf{x}} \mathbb{P}(s_{\mathbf{x}} \dots s_{\mathbf{y}}, t) d\mathbf{y} d\mathbf{x} \quad (2.7)$$

Introducing orthonormal basis  $|s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle$  and field operators  $\hat{a}(\mathbf{x})^\dagger, \hat{a}(\mathbf{x})$  that add/remove particles to/from location  $\mathbf{x}$  as we did in Section 1.2.1 for the Chemical Master Equation, allows us to represent diffusion as Hamiltonian  $\hat{\mathcal{D}}$  acting on a linear state space  $|\Psi(t)\rangle$ .

$$\mathbb{I} \partial_t |\Psi(t)\rangle = \hat{\mathcal{D}} |\Psi(t)\rangle \quad \text{where} \quad |\Psi(t)\rangle := \sum_{s_{\mathbf{x}} \dots s_{\mathbf{y}} \in \mathbb{N}} \mathbb{P}(s_{\mathbf{x}} \dots s_{\mathbf{y}}, t) |s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle \quad (2.8)$$

$$\hat{\mathcal{D}} = -\frac{\mathbb{I} D}{2} \int_{\mathbb{R}^M} \int_{\partial \mathbf{x}} (\hat{a}(\mathbf{y}) - \hat{a}(\mathbf{x}))^\dagger (\hat{a}(\mathbf{y}) - \hat{a}(\mathbf{x})) d\mathbf{y} d\mathbf{x} \quad (2.9)$$

### 2.1.3 Reaction-Diffusion Hamiltonian

Finally by extending the state space  $|s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle$  to multiple particle species  $s_{\mathbf{x}} \in \mathbb{N}^S, \mathbf{x} \in \mathbb{R}^M$  we may bring together the contributions from reaction and diffusion. In order to simplify results we can vectorise the field operators  $\hat{a}(\mathbf{x}), \hat{a}(\mathbf{x})^\dagger$  such that their  $i$ th components are the field operators for particle species  $i$ . Note that  $^\dagger$  acts on the operator and  $^\top$  acts on the vector, which may lead to inner or outer products.

$$\begin{aligned} \hat{a}(\mathbf{x}) |s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle &:= s_{\mathbf{x}} |s_{\mathbf{x}} - 1 \dots s_{\mathbf{y}}\rangle & [\hat{a}(\mathbf{x}), \hat{a}(\mathbf{y})^{\dagger\top}] &= \mathbb{1}\delta(\mathbf{x} - \mathbf{y}) \\ \hat{a}(\mathbf{x})^\dagger |s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle &:= |s_{\mathbf{x}} + 1 \dots s_{\mathbf{y}}\rangle & [\hat{a}(\mathbf{x}), \hat{a}(\mathbf{y})^\top] &= [\hat{a}(\mathbf{x})^\dagger, \hat{a}(\mathbf{y})^{\dagger\top}] = 0 \\ \hat{a}(\mathbf{x})^\dagger \hat{a}(\mathbf{x}) |s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle &= s_{\mathbf{x}} |s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle \end{aligned} \quad (2.10)$$

The diffusion coefficients for each species are now the elements of diagonal matrix  $\mathbf{D}$  and reaction rates  $\lambda(\gamma, \mathbf{x})$  may also acquire spatial dependence. The state  $|\Psi(t)\rangle$  now spans  $\mathbb{N}^S \times \mathbb{R}^M$ . We have also rewritten the products of operators in the reaction term as exponentiated inner products  $\gamma^\top \ln \hat{a}(\mathbf{x})^\dagger = \sum_{i=1}^S \gamma[i] \ln \hat{a}_i(\mathbf{x})^\dagger$ .

$$\mathbb{i} \partial_t |\Psi(t)\rangle = \int_{\mathbb{R}^M} \hat{\mathcal{H}}(\mathbf{x}) d\mathbf{x} |\Psi(t)\rangle \quad \text{where} \quad |\Psi(t)\rangle := \sum_{s_{\mathbf{x}} \dots s_{\mathbf{y}} \in \mathbb{N}^S} \mathbb{P}(s_{\mathbf{x}} \dots s_{\mathbf{y}}, t) |s_{\mathbf{x}} \dots s_{\mathbf{y}}\rangle \quad (2.11)$$

$$\hat{\mathcal{H}}(\mathbf{x}) = \mathbb{i} \sum_{\langle \gamma, g \rangle \in \Gamma} \lambda(\gamma, \mathbf{x}) \left( e^{\gamma^\top \ln \hat{a}(\mathbf{x})^\dagger} - \mathbb{1} \right) e^{g^\top (\ln \hat{a}(\mathbf{x})^\dagger + \ln \hat{a}(\mathbf{x}))} \quad (2.12)$$

$$- \frac{\mathbb{i}}{2} \int_{\partial \mathbf{x}} (\hat{a}(\mathbf{y})^\dagger - \hat{a}(\mathbf{x})^\dagger)^\top \mathbf{D} (\hat{a}(\mathbf{y}) - \hat{a}(\mathbf{x})) d\mathbf{y} \quad (2.13)$$

## 2.2 Green's Functions

### 2.2.1 Non-unitary Evolution Operator

Solving (2.11) formally suggests we define a non-unitary time independent evolution operator  $\hat{\mathcal{U}}(t, t')$ . In the ordinary quantum cases this operator is unitary; we will have to keep this in mind when applying the following methods.

$$\begin{aligned} \hat{\mathcal{U}}(t, t') &:= e^{-\mathbb{i}(t-t') \int \hat{\mathcal{H}}(\mathbf{x}) d\mathbf{x}} & \hat{\mathcal{U}}(t, t')^\dagger \hat{\mathcal{U}}(t, t') &\neq \mathbb{1} \\ & & \hat{\mathcal{H}}(\mathbf{x})^\dagger &\neq \hat{\mathcal{H}}(\mathbf{x}) \end{aligned} \quad (2.14)$$

### 2.2.2 Dynamical Ensemble Averages

Since the coefficients of state vector  $|\Psi(t)\rangle$  directly yield probabilities,  $\mathbb{P}(s_{\mathbf{x}} \dots s_{\mathbf{y}}, t)$  not probability amplitudes, ensemble averages  $\langle A(\mathbf{x}, t) \rangle$  are calculated with a differently defined density matrix  $\hat{\rho}(t)$ . One of the states in the outer product  $\langle \Psi(t) |$  is replaced by the unit projection state  $\langle \mathbb{P} |$ . This state can be written in terms of field operators; in fact it is the left eigenstate of the creation operator — a coherent state.

$$\langle A(\mathbf{x}, t) \rangle = \text{Tr} \left[ \hat{\rho}(t) \hat{\mathcal{A}}(\mathbf{x}, t) \right] \quad \text{where} \quad \hat{\rho}(t) := |\Psi(t)\rangle \langle \mathbb{P}| \quad (2.15)$$

$$\begin{aligned} \langle \mathbb{P} | &:= \sum_{s_{\mathbf{x}} \dots s_{\mathbf{y}} \in \mathbb{N}^S} \langle s_{\mathbf{x}} \dots s_{\mathbf{y}} | \\ &= \langle \emptyset | e^{\int d\hat{a}(\mathbf{x})} \end{aligned} \quad \langle \mathbb{P} | \hat{a}(\mathbf{x})^\dagger = \langle \mathbb{P} | \quad (2.16)$$

This modified definition of  $\hat{\rho}(t)$  leads to a Liouville Equation and Ehrenfest Theorem that do not involve commutators. Furthermore, the time evolved density matrix no longer has  $\hat{\mathcal{U}}(t, t')$  acting on both sides.

$$\overrightarrow{d} \hat{\rho}(t) = \hat{\mathcal{H}} \hat{\rho}(t) \quad \overrightarrow{d} \hat{\mathcal{A}}(\mathbf{x}, t) = \mathbb{I} \partial_t \hat{\mathcal{A}}(\mathbf{x}, t) + \hat{\mathcal{A}}(\mathbf{x}, t) \hat{\mathcal{H}} \quad (2.17)$$

### 2.2.3 The Heisenberg Picture

In the interacting picture the time dependance is shared between the observable  $\hat{\mathcal{A}}(\mathbf{x}, t)$  and density  $\hat{\rho}(t)$ . Transforming out the time dependance from the density into the operator using (2.14) brings the operator into the Heisenberg picture  $\hat{\mathcal{A}}_H(\mathbf{x}, t)$ . Letting the evolution  $\hat{\mathcal{U}}(t) := \hat{\mathcal{U}}(t, 0)$  and the initial condition  $\hat{\rho} := \hat{\rho}(0)$  we can write

$$\langle A(\mathbf{x}, t) \rangle = \text{Tr} \left[ \hat{\rho} \hat{\mathcal{A}}_H(\mathbf{x}, t) \right] \quad \hat{\mathcal{A}}_H(\mathbf{x}, t) := \hat{\mathcal{A}}(\mathbf{x}, t) \exp \left[ -\mathbb{I} t \int_{\mathbb{R}^M} \hat{\mathcal{H}}(\mathbf{x}) d\mathbf{x} \right] \quad (2.18)$$

This allows an arbitrary choice for the density matrix, and focuses the dynamics onto the operators. Commutators (2.10) at equal times remain the same, and time-independent operators like  $\hat{a}(\mathbf{x})$  and  $\hat{a}(\mathbf{x})^\dagger$  pick up a time dependence from the evolution operator.

### 2.2.4 Green's Functions & the Hierarchy

Since both the Hamiltonian and any observable operator can be expressed in terms of vector field operators  $\hat{a}(\mathbf{x})$  and  $\hat{a}(\mathbf{x})^\dagger$ , all dynamical ensemble averages (2.18) are expressed in terms of strings of field operators. It seems natural to attempt defining a building block out of which one can express these averages. These objects are known as Green's Functions and encode all correlations and responses of the system.

$$\mathbf{G}(\mathbf{x}, t | \mathbf{y}, t') := \frac{1}{\hbar} \langle \mathcal{T} \{ \hat{a}(\mathbf{x}, t) \hat{a}(\mathbf{y}, t')^{\dagger\top} \} \rangle \quad (2.19)$$

$\hat{a}(\mathbf{x}, t)$  and  $\hat{a}(\mathbf{y}, t')^\dagger$  are implicitly in the Heisenberg picture

$\mathcal{T}$  is the time-ordering meta operator

Above is what is known as a one-particle Green's Function. Substituting this into the Ehrenfest Theorem (2.17) leads to two-particle Green's Functions. This is due to the nasty way in which the time derivative and time ordering meta-operator interact. Repeated substitution of these objects reveals that  $n$ -particle Green's Function is coupled to  $n \pm 1$  particle Green's Functions. This infinite set of coupled differential equations is called the Martin-Schwinger Hierarchy [5]. The time ordering operator  $\mathcal{T}\{ \cdot \}$  is evaluated to obtain explicit expressions for Green's Function in terms of greater/lesser and retarded/advanced components. We drop the spatial dependence  $\mathbf{x}$  to avoid clutter.

$$\overset{\text{Greater and Lesser Components}}{\mathbf{G}(z, z')} = \theta(z, z') \mathbf{G}^>(z, z') + \theta(z', z) \mathbf{G}^<(z, z') \quad (2.20)$$

$$\overset{\text{Retarded / Advanced Components}}{\mathbf{G}^\pm(t, t')} = \pm \theta(\pm(t - t')) \left( \mathbf{G}^>(t, t') - \mathbf{G}^<(t, t') \right) \quad (2.21)$$

$$\overset{\text{Antisymmetry}}{\mathbf{G}^\pm(t, t')^\dagger} = -\mathbf{G}^\mp(t', t) \quad \overset{\text{Causality}}{\mathbf{G}^\pm(t, t')^\dagger} = \mathbf{G}^\mp(t', t) \quad (2.22)$$

Here  $\theta(t - t')$  and  $\theta(z, z')$  are the Heaviside Step Functions which are nonzero for real  $t > t'$  and complex  $z > z'$  time arguments respectively. These Green's Function possess useful symmetries: anti-symmetry inherited from fermion behaviour and another condition encoding causality. The use of Langreth Rules [5] allows to conversion of contour integrals into real integrals.

### 2.2.5 Noninteracting Equations of Motion

Suppose the hamiltonian  $\mathbf{h}(t)$  only has quadratic terms in  $\hat{a}(\mathbf{x}), \hat{a}(\mathbf{x})^\dagger$ . This is effectively a non-interacting case and decouples the one-particle equation of motion from the hierarchy revealing that the Green's Function is the wavefunction solution to the Schrödinger Equation with a dirac delta excitation in the field. Presented are the set of conjugate equations in single particle orbital matrix form, where the derivative acts on the right and left times respectively. Here  $\mathbf{I}$  is the identity matrix.

$$\left[ \frac{\overrightarrow{d}}{dt} - \mathbf{h}(t) \right] \mathbf{G}(t, t') = \mathbf{e}(t, t') \quad \mathbf{G}(t, t') \left[ -\frac{\overleftarrow{d}}{dt'} - \mathbf{h}(t') \right] = \mathbf{e}(t, t') \quad (2.23)$$

$$\text{where } \mathbf{e}(t, t') = \mathbf{I} \delta(t, t') \quad [\mathbf{h}(t)]_{i,j} = \langle i | \hat{h}(t) | j \rangle$$

### 2.2.6 The Dyson Equation

Using complex convolutions on the Keldysh Contour  $\gamma$ , inverses and group properties that the Green's Functions obey, its possible to get rid of the time derivative in the equations of motion (2.23) and derive the Dyson Equation. This formula expresses the coupled Green's Function  $\mathbf{G}(t, t')$  in terms of the isolated Green's Function  $\mathbf{g}(t, t')$ , which is obtained by considering the diagonal elements of  $\mathbf{h}(t)$  only. These are convoluted with the self-energy  $\Sigma(t, t')$ , which can not always be expressed explicitly, but still obeys the same symmetry properties (2.22) as the Green's Functions. The convolution variables match up in the same way matrix multiplication indexes do.

$$\mathbf{G}(t, t') = \mathbf{g}(t, t') + \mathbf{g} \circ \Sigma \circ \mathbf{G}(t, t') = \mathbf{g}(t, t') + \mathbf{G} \circ \Sigma \circ \mathbf{g}(t, t') \quad (2.24)$$

$$\text{where } \mathbf{a} \circ \mathbf{b}(t, t') = \int_{\gamma} \mathbf{a}(t, \tau) \mathbf{b}(\tau, t') d\tau \quad \Sigma(t, t') \text{ is the self-energy}$$

### 2.2.7 The Keldysh Equation

The analogue of the Dyson equation, projected into greater/lesser and retarded/advanced subspace, done readily with the help of Langreth Rules, is known as the Keldysh Equation. This equation is used to investigate the steady state behaviour.

$$\mathbf{G}^{\lessgtr}(t, t') = \underbrace{(\mathbf{e} + \mathbf{G}^+ \bullet \Sigma^+)}_{\text{Transient Term}} \bullet \mathbf{g}^{\lessgtr} \bullet \underbrace{(\mathbf{e} + \Sigma^- \bullet \mathbf{G}^-)}_{\text{Steady State Term}}(t, t') + \mathbf{G}^+ \bullet \Sigma^{\lessgtr} \bullet \mathbf{G}^-(t, t') \quad (2.25)$$

$$\text{where } \mathbf{a} \bullet \mathbf{b}(t, t') = \int_{t_0}^{\infty} \mathbf{a}(t, \tau) \mathbf{b}(\tau, t') d\tau$$

### 2.2.8 Time Independent Steady State Regime

The Hamiltonian is time independent  $\mathbf{h}(t) = \mathbf{h}$  if all external influences are also time independent. This makes all Green's Functions components  $\mathbf{G}^X(t, t')$  - among which are the advanced/retarded and greater/lesser components - depend on real time differences  $\tau = t - t'$ , and the time translation invariance allows their representations in fourier space.

$$\overset{\text{Component Fourier Transforms}}{\mathbf{G}^X(\omega) = \int_{-\infty}^{\infty} \mathbf{G}^X(\tau) e^{i\omega\tau} d\tau \quad \mathbf{G}^X(t, t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathbf{G}^X(\omega) e^{-i\omega(t-t')} d\omega} \quad (2.26)$$

Note that convolution  $\bullet$  as defined in equation (2.25) reduces to regular fourier convolution if  $t_0 = -\infty$  ; this puts the dynamics far from initial conditions, in the steady state regime. According to the convolution theorem, applying the fourier transform  $\mathcal{F}[\cdot]$  to convolutions of two functions retrieves the product of their individual fourier transforms. The Keldysh Equation (2.25) yields another powerful simplification.

$$\overset{\text{Time Independent Relations}}{\mathbf{G}^+(\omega) - \mathbf{G}^-(\omega) = \mathbf{G}^>(\omega) - \mathbf{G}^<(\omega)} \quad (2.27)$$

$$\overset{\text{Steady State Convolution}}{\mathcal{F}[\mathbf{a} \bullet \mathbf{b}(t, t')] = \mathbf{A}(\omega)\mathbf{B}(\omega)} \quad \Rightarrow \quad \overset{\text{Steady State Keldysh Equation}}{\mathbf{G}^{\gtrless}(\omega) = \mathbf{G}^+(\omega)\mathbf{\Sigma}^{\gtrless}(\omega)\mathbf{G}^-(\omega)}$$

### 3 Model Systems

#### 3.1 Lotka–Volterra

The Lotka–Volterra model is a canonical example of a predator-prey dynamical system. Here we may summarise the reactive behaviour between predators  $A(t)$  and prey  $B(t)$  in Feynman diagrams. Particles are represented by arrows  $\rightarrow$  and reactions by wavy arrows  $\rightsquigarrow$ .

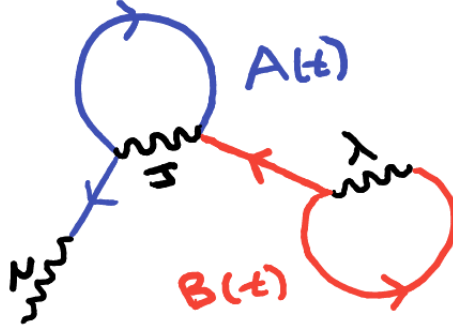


Figure 5: Feynman diagram of the Lotka–Volterra field  $\begin{pmatrix} A \\ B \end{pmatrix}$  revealing autocatalytic birth rate  $\lambda$  for prey, constant death rate  $\mu$  for predators and predator–prey interaction  $J$

Letting  $s(t) = \begin{pmatrix} A \\ B \end{pmatrix}$ , the stoichiometric matrix  $\mathbf{\Gamma}$  and propensity  $\omega(s|\mathbf{\Gamma})$  are determined from the state changes  $\gamma$  and the rates of each reaction  $\sigma(\gamma) = \mu, \lambda, J$ . It can easily be seen that the mean field approximation (1.6) now yields the well-known equations.

$$\mathbf{\Gamma} = \begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & -1 \end{pmatrix} \quad \omega(s|\mathbf{\Gamma}) = \begin{pmatrix} \mu A(t) \\ \lambda B(t) \\ J A(t) B(t) \end{pmatrix} \quad (3.1)$$

Figure 6 reveals that this reaction topology produces nullclines that intersect to form a stable limit cycle. The amplitude is governed by the initial conditions and time period by the death and birth rates. According to the reaction term (2.6) the Hamiltonian for predator field  $\hat{a}$  and prey field  $\hat{b}$  is

$$\mathcal{R} = \mathbb{I} \left( \mu(1 - \hat{a}^\dagger)\hat{a} + \lambda(\hat{b}^{\dagger 2} - \hat{b}^\dagger)\hat{b} + J(\hat{a}^{\dagger 2} - \hat{a}^\dagger\hat{b}^\dagger)\hat{a}\hat{b} \right) \quad (3.2)$$

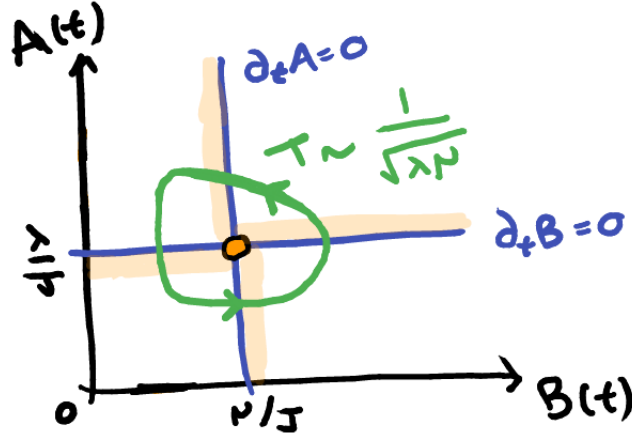


Figure 6: Predator–prey field nullclines intersecting at unstable fixed point giving rise to stable limit cycle whos time period  $T \sim 1/\sqrt{\lambda\mu}$

### 3.2 Michaelis–Menten

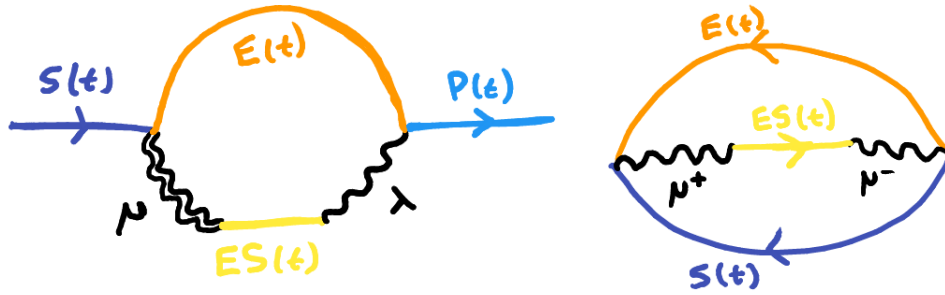


Figure 7: Feynman diagram of the Michaelis–Menten field  $(S, E, ES, P)$  showing reversible substrate–enzyme reaction  $\mu$  and irreversible complex to product reaction  $\lambda$

## References

- [1] D. T. Gillespie, “A rigorous derivation of the chemical master equation,” *Physica A: Statistical Mechanics and its Applications*, vol. 188, pp. 404–425, 9 1992.
- [2] D. T. Gillespie, “Stochastic Simulation of Chemical Kinetics,” *Annu. Rev. Phys. Chem*, vol. 58, pp. 35–55, 2007.



- [3] J. Halatek and E. Frey, “Rethinking pattern formation in reaction–diffusion systems,” *Nature Physics*, p. 1, 2 2018.
- [4] M. Doi, “Second quantization representation for classical many-particle system,” *J. Phys. A: Math. Gen*, vol. 9, no. 9, 1976.
- [5] G. Stefanucci and R. van Leeuwen, *Nonequilibrium Many-Body Theory of Quantum Systems*, vol. 54. Cambridge University Press, 2013.

## A Chemical Master Equation

The Chemical Master Equation is a specific case of the differential form of the Chapman-Kolmogorov equation, which in turn is a consequence of the Markov property and considering transitions rates at infinitesimal time intervals. Starting with the law of total probability

$$\mathbb{P}(s, t + dt) = \sum_{s'} \mathbb{P}(s, t + dt | s', t) \mathbb{P}(s', t) \quad (\text{A.1})$$

and probability of state change in a small interval  $dt$

$$\mathbb{P}(s, t + dt | s', t) = \delta(s - s') \left( 1 - \sum_{r=1}^R \omega(r | s') dt \right) + \sum_{r=1}^R \delta(s - s' - \mathbf{\Gamma}[r]) \omega(r | s') dt \quad (\text{A.2})$$

where the first term is the probability of no reaction occurring, and the second term restricts the possible state changes to those given by the stoichiometric matrix  $\mathbf{\Gamma}$ . Upon substitution into the total law of probability the Kronecker deltas  $\delta$  filter the sum over  $s'$  leaving

$$\mathbb{P}(s, t + dt) - \mathbb{P}(s, t) = \sum_{r=1}^R \omega(r | s - \mathbf{\Gamma}[r]) dt \mathbb{P}(s - \mathbf{\Gamma}[r], t) - \omega(r | s) dt \mathbb{P}(s, t)$$

Dividing by  $dt$  and indentifying the time derivative on the left hand side recovers (1.4). Now to get the equation for the first moment  $\langle s \rangle$  we multiply by  $s$  and sum over sets  $\mathbb{N}^S$

$$\begin{aligned} \sum_{s \in \mathbb{N}^S} \partial_t \mathbb{P}(s, t) s &= \sum_{s \in \mathbb{N}^S} \sum_{r=1}^R \omega(r|s - \mathbf{\Gamma}[r]) \mathbb{P}(s - \mathbf{\Gamma}[r], t) s - \omega(r|s) \mathbb{P}(s, t) s \\ \partial_t \sum_{s \in \mathbb{N}^S} \mathbb{P}(s, t) s &= \sum_{r=1}^R \sum_{s \in \mathbb{N}^S} \omega(r|s) \mathbb{P}(s, t) (s + \mathbf{\Gamma}[r]) - \omega(r|s) \mathbb{P}(s, t) s \\ \partial_t \langle s \rangle &= \sum_{r=1}^R \mathbf{\Gamma}[r] \langle \omega(r|s) \rangle \end{aligned}$$

Recognising the matrix-vector multiplication with the stoichiometric matrix prompts us to vectorise the propensity  $\omega(s|\mathbf{\Gamma}) \in [0, \infty)^R$ . The nonlinear propensity couples to higher order moments, unfolding the heirarchy (1.5).

## B Doi Representation

Using the defining action of the field operators (2.1) it is possible to verify the bosonic commutation relations, the operator representation of propensity and shifts in state space.

### B.1 Commutation Relations

$$\begin{aligned} (\hat{a}_i \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_i) |s\rangle &= (s[i] + \delta_{ij} - s[i]) |s + \mathbb{1}_j - \mathbb{1}_i\rangle \\ &= \delta_{ij} |s + \mathbb{1}_j - \mathbb{1}_i\rangle \end{aligned}$$

$$\begin{aligned} (\hat{a}_i^\dagger \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_i^\dagger) |s\rangle &= (1 - 1) |s + \mathbb{1}_j + \mathbb{1}_i\rangle \\ &= 0 \end{aligned}$$

$$\begin{aligned} (\hat{a}_i \hat{a}_j - \hat{a}_j \hat{a}_i) |s\rangle &= ((s[i] - \delta_{ij})s[j] - (s[j] - \delta_{ij})s[i]) |s - \mathbb{1}_j - \mathbb{1}_i\rangle \\ &= \delta_{ij} (s[i] - s[j]) |s - \mathbb{1}_j - \mathbb{1}_i\rangle \\ &= 0 \end{aligned}$$

## B.2 Propensity

Note that repeated application of the annihilation operator brings out combinatorial factors, and subsequent application of the creation operator can bring back the ket to its original state without further factors coming out

$$\begin{aligned}
\hat{a}_i^n |s\rangle &= (s[i] - n + 1) \dots (s[i] - 1) s[i] |s - n\mathbb{1}_i\rangle \\
&= \frac{s[i]!}{(s[i] - n)!} |s - n\mathbb{1}_i\rangle \\
&= n! \binom{s[i]}{n} |s - n\mathbb{1}_i\rangle \\
\implies \frac{1}{n!} \hat{a}_i^{\dagger n} \hat{a}_i^n |s\rangle &= \binom{s[i]}{n} |s\rangle
\end{aligned} \tag{B.1}$$

Knowing the eigenstate operator representation of the combinatoric factor involving  $s[i]$  and letting  $\hat{\omega}(r) |s\rangle = \omega(r|s) |s\rangle$ , we can see from the general form of the propensity (1.2) that

$$\hat{\omega}(r) = \sigma[r] \prod_{i=1}^S \frac{\hat{a}_i^{\dagger g[i,r]} \hat{a}_i^{g[i,r]}}{g[i,r]!}$$

We note that the products of  $g[i,r]!$  simply renormalise the reaction rate  $\sigma[r]$  suggesting we define renormalised propensity  $\lambda[r]$  recovering equations (2.3). We also note that it is possible to express the product over species  $i$  in a compact form as a normal ordered inner product

$$\hat{\omega}(r) = \lambda[r] \mathfrak{e}^{g(r)^\top (\ln \hat{a}^\dagger + \ln \hat{a})} \tag{B.2}$$

$$\text{where } \hat{a} = (\hat{a}_1 \dots \hat{a}_S) \quad g(r) = (g[1,r] \dots g[S,r]) \tag{B.3}$$

## B.3 Shifts

Noting that while there exists no inverse of the annihilation operator — since it is not possible to account for the case when  $s[i] = 0$  — the creation operator has a simple inverse

$$\begin{aligned}
\hat{a}_i^{-\dagger} \hat{a}_i^\dagger |s\rangle &:= |s\rangle \\
&= \hat{a}_i^{-\dagger} |s + \mathbb{1}_i\rangle \implies \hat{a}_i^{-\dagger} |s\rangle = |s - \mathbb{1}_i\rangle
\end{aligned}$$

and hence (2.4) is easily verified.

## B.4 Reaction Term

Suppose we define a state vector spanning the space of all possible states  $s \in \mathbb{N}^S$ . Inspired by quantum mechanics, we let the coefficients of this vector be probability  $\mathbb{P}(s, t)$  as given by definition (2.5) and derive its equation of motion

$$\begin{aligned}
\partial_t |\Psi(t)\rangle &= \sum_{s \in \mathbb{N}^S} \partial_t \mathbb{P}(s, t) |s\rangle \\
&= \sum_{s \in \mathbb{N}^S} \sum_{r=1}^R \omega(r|s - \mathbf{\Gamma}[r]) \mathbb{P}(s - \mathbf{\Gamma}[r], t) |s\rangle - \omega(r|s) \mathbb{P}(s, t) |s\rangle \\
&= \sum_{r=1}^R \sum_{s \in \mathbb{N}^S} \omega(r|s) \mathbb{P}(s, t) |s + \mathbf{\Gamma}[r]\rangle - \hat{\omega}(r) \sum_{s \in \mathbb{N}^S} \mathbb{P}(s, t) |s\rangle \\
&= \sum_{r=1}^R \prod_{i=1}^S \hat{a}_i^{\dagger \Gamma[i, r]} \sum_{s \in \mathbb{N}^S} \omega(r|s) \mathbb{P}(s, t) |s\rangle - \hat{\omega}(r) \sum_{s \in \mathbb{N}^S} \mathbb{P}(s, t) |s\rangle \\
&= \sum_{r=1}^R \left( \prod_{i=1}^S \hat{a}_i^{\dagger \Gamma[i, r]} - \hat{\mathbb{1}} \right) \hat{\omega}(r) \sum_{s \in \mathbb{N}^S} \mathbb{P}(s, t) |s\rangle
\end{aligned}$$

Identifying the state vector  $|\Psi(t)\rangle$  on the right-hand-side and multiplying by the imaginary factor  $\mathfrak{i}$  recovers the Hamiltonian (2.6).