

Lecture 26: chemical kinetics in spin systems

An important change of perspective is in order before we proceed with the description of chemical processes in spin systems: we would find it very convenient to think about the *transport and flux of magnetization* within a topologically fixed spin system rather than consider moving spins.

We shall skip the Bloch and MacConnell equations here (it is assumed that you have either seen them already or would easily see through them, since they are quite simple and lack general applicability).

Chemical reaction networks

The law of the conservation of matter for a network of unidirectional reactions between substances A_k may be described by the following system of linear equations:

$$\begin{pmatrix} \nu_{11} & \cdots & \nu_{1n} \\ \vdots & \ddots & \vdots \\ \nu_{n1} & \cdots & \nu_{nn} \end{pmatrix} \begin{pmatrix} [A_1] \\ \vdots \\ [A_n] \end{pmatrix} = \mathbf{N}\vec{A} = 0$$

where the *stoichiometric matrix* \mathbf{N} contains the coefficients for the chemical reactions. It is convenient to separate it nominally into the “reactant” and the “product” submatrices: $\mathbf{N} = \mathbf{N}_+ - \mathbf{N}_-$. We can also define the extent $\xi_k(t)$ to which the reaction k has proceeded by time t as:

$$\vec{A}(t) = \vec{A}(0) + \mathbf{N}\vec{\xi}(t)$$

The reaction rates are then related to the extents by the mass-action law:

$$\frac{d}{dt}\vec{A}(t) = \mathbf{N}\frac{d}{dt}\vec{\xi}(t) = \mathbf{N} \begin{pmatrix} k_1 \prod_{m=1}^n [A_m]^{\nu_{1m}^+} \\ \vdots \\ k_n \prod_{m=1}^n [A_m]^{\nu_{nm}^+} \end{pmatrix}$$

This is very non-linear and only soluble analytically if there is just one term in the products, *i.e.* for networks of first-order chemical processes, where:

$$\frac{d}{dt}[A_j] = \sum_{m=1}^n k_{jm}[A_m] \quad \Rightarrow \quad \frac{d}{dt}\vec{A}(t) = \mathbf{K}\vec{A}(t) \quad \Rightarrow \quad \vec{A}(t) = \exp(\mathbf{K}t)\vec{A}(0)$$

(with the condition on the diagonal elements of \mathbf{K} to balance out the off-diagonal elements so that the law of the conservation of matter is obeyed).

Networks of first-order reactions

When magnetization is pumped over from site n to site m in a spin system, the state populations are pumped across between the following states:

$$\dots \otimes \hat{L}_\alpha^{(n)} \otimes \dots \quad \rightarrow \quad \dots \otimes \hat{L}_\alpha^{(m)} \otimes \dots$$

where α is an index running over the elements of the spin state space. So the task of constructing a superoperator that would perform this action amounts to subtracting a slice of the population from $\langle \dots \otimes \hat{L}_\alpha^{(n)} \otimes \dots \rangle$ and forwarding it to $\langle \dots \otimes \hat{L}_\alpha^{(m)} \otimes \dots \rangle$:

$$\hat{K} = k_{mn} \left(|\hat{L}_\alpha^{(m)}\rangle\langle\hat{L}_\alpha^{(n)}| - |\hat{L}_\alpha^{(n)}\rangle\langle\hat{L}_\alpha^{(n)}| \right)$$

the superoperator in brackets is known as the *rearrangement superoperator* – it shifts the population from one state of the spin system to another.

The policy on chemical transport of multi-spin orders is case-dependent. In principle, the coherence with any observer spins must be preserved during chemical exchange, that is:

$$\dots \otimes S \otimes \dots \otimes \hat{L}_\alpha^{(n)} \otimes \dots \quad \rightarrow \quad \dots \otimes S \otimes \dots \otimes \hat{L}_\alpha^{(m)} \otimes \dots$$

and, so long as we are treating a single system (or an ensemble of systems, which have chemical exchange happening inside them), this should be taken into account. In a typical solution, however, this would lead to the emergence of inter-molecular coherences between identical molecules – a situation that density matrix formalism is ill-equipped to accommodate. Furthermore, since such coherences are always non-observable and the spin is very unlikely to jump back to the exact molecule that it originally came from, the coherences in question are usually counted as “lost”:

$$\hat{K} = -k_{mn} |\hat{S} \otimes \hat{L}_\alpha^{(n)}\rangle\langle\hat{S} \otimes \hat{L}_\alpha^{(n)}|$$

and the corresponding contribution to the kinetics superoperator effectively causes relaxation.