Here I will summarize certain mathematical properties of the master equation

$$\frac{dp_i}{dt} = -\sum_{j \neq i} k_{i \to j} p_i + \sum_{j \neq i} k_{j \to i} p_j. \quad (1)$$

This equation describes the time evolution of a stochastic system that can occupy any of its $N$ states, which are labeled by indices $i, j = 1, 2, ..., N$. The probability of finding the system in state $i$ at time $t$ is given by $p_i(t)$. The properties of the system are completely specified by the initial conditions $p_i(0)$ and by the set of rate coefficients $k_{i \to j}$ between each pair of states. Of course, not all of the rate coefficients have to be nonzero. I will, however, assume that all the states are “connected” in that, for any pair of states $i$ and $j$, there is a sequence of intermediate states, $i_1, i_2, ..., i_M$ such that the rate coefficients $k_{i \to i_1}, k_{i_1 \to i_2}, ..., k_{i_M \to j}$ are nonzero. In other words, it is possible to arrive in any state $j$, having started from any state $i$, either directly or through a sequence of intermediate states. If this is not the case then it makes sense to break all the states into the subsets of connected states. The dynamics within each subset is then completely decoupled from that of all other subsets and so each subset can be studied separately.

I will further assume that the rate coefficients satisfy the detailed balance condition:

$$k_{i \to j} p_i^{(eq)} = k_{j \to i} p_j^{(eq)}, \quad (2)$$

where $p_i^{(eq)}$ is the equilibrium population of state $i$. The master equation can be rewritten in a matrix form:

$$\frac{dp}{dt} = -Kp, \quad (3)$$

where $p$ is a column vector with components $p_i$ and $K$ is a square matrix, whose elements are given by $K_{ij} = -k_{j \to i}$ for $j \neq i$ and $K_{ii} = \sum_{j \neq i} k_{i \to j}$. The solution of this equation can be written as

$$p(t) = T(t)p(0), \quad (4)$$

where the transition matrix $T$ is equal to the matrix exponent

$$T(t) = \exp(-Kt) \quad (5)$$
Consider the probability $p_i(t)$ to find the system in state $i$ at time $t$. According to Eq.4, this can be written as

$$p_i(t) = \sum_j T_{ij}(t)p_j(0),$$

allowing us to interpret the matrix elements $T_{ij}(t)$ as the conditional probabilities to find the system in a state $i$ at time $t$ provided that it was in state $j$ at time 0.

If the transition matrix $T$ is known, the rate coefficients of the underlying master equation can be recovered by using the following relation:

$$k_{i \to j} = \lim_{t \to 0^+} dT_{ji}(t)/dt \quad (6)$$

This result is readily proven by expanding Eq.5 in a Taylor series in $t$ and using the above definition of matrix $K$. This expression formalizes our definition of a rate coefficient as transition probability per unit time. We will use it later to obtain rate coefficients from molecular trajectories.

Introducing the eigenvectors $u_\alpha$ and eigenvalues $\lambda_\alpha$ of the matrix $K$, defined by the equation

$$K u_\alpha = \lambda_\alpha u_\alpha, \quad (7)$$

we can also write the solution of the master equation as a spectral expansion,

$$p(t) = \sum_\alpha c_\alpha \exp(-\lambda_\alpha t)u_\alpha, \quad (8)$$

where the coefficients $c_\alpha$ are determined by the initial condition. On important property of the eigenvalues $\lambda_\alpha$ is that they are real numbers. To show this, consider one of the eigenvalues $\lambda$ and the corresponding eigenvector $u$ and rewrite Eq.7 explicitly as follows:

$$\sum_j K_{ij}u_j = \lambda u_i \quad (9)$$

Now define a rescaled matrix

$$\tilde{K}_{ij} = \frac{K_{ij}p_j^{(eq)}}{\sqrt{p_i^{(eq)}p_j^{(eq)}}}$$

and rescaled eigenvector $v_j = u_j/\sqrt{p_j^{(eq)}}$. In terms of those, the above eigenvalue equation can be rewritten as

$$\sum_j \tilde{K}_{ij}v_j = \lambda v_i$$
Therefore, $\lambda$ is also an eigenvalue of the rescaled matrix $\tilde{K}$. In view of the detailed balance condition, Eq.2, the rescaled matrix $\tilde{K}$ is symmetric and so the eigenvalue $\lambda$ is a real number. This, in particular, implies that our master equation cannot have oscillatory solutions.

Further physical constraints on the eigenvalues $\lambda_{\alpha}$ come from two physical requirements. Firstly, the probabilities $p_i$ are nonnegative numbers that cannot exceed one. Thus negative values $\lambda_{\alpha}$ are unphysical, as, according to Eq.8, they would lead to exponentially growing probabilities. Secondly, all $\lambda_{\alpha}$’s cannot be positive because, according to Eq.8, this would make all probabilities vanish in the limit $t \to \infty$, a result that would contradict the assertion that the system is always found in one of the $N$ states and so the probabilities $p_i$ must add up to one at any time $t^1$. Instead, in the limit $t \to \infty$ the populations of states should be approaching their equilibrium values, i.e., $p_i(\infty) = p_i^{(eq)}$. Therefore, one of the $\lambda_{\alpha}$’s, say the one corresponding to $\alpha = 0$, must be equal to zero, $\lambda_0 = 0$. The corresponding eigenvector $u_0$ is, to within a constant normalization factor, given by

$$u_0 = (p_1^{(eq)}, p_2^{(eq)}, ..., p_N^{(eq)})^T.$$  

Indeed, substituting $p = u_0$ into the rhs of Eq.3 results in the identity $d\mathbf{p}/dt = 0$, as anticipated for equilibrium probabilities.

Finally, consider any quantity (e.g. position etc.) $x$ that takes on discrete values $x = x_1, x_2, ..., x_N$ when the system is, respectively, in states $i = 1, 2, ..., N$. The trajectory $x(t)$ is therefore a piecewise function that remains constant as long as the system remains in the same state. Computation of the correlation functions of the form $\langle x(0)x(t) \rangle$ is a commonly encountered problem. For a system obeying the above master equation, this correlation function can be calculated as

$$\langle x(0)x(t) \rangle = \sum_{i,j} x_j T_{ji}(t) x_i p_i^{eq} = \mathbf{x}^T e^{-\mathbf{K}t} \tilde{x},$$

where $\tilde{x}$ is the column-vector with the components $(x_1p_1^{eq}, x_2p_2^{eq}, ..., x_Np_N^{eq})$.

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1The fact that the sum of the probabilities $P(t) = \sum_i p_i(t)$ is conserved is readily proven by considering its time derivative $dP/dt = \sum_i dp_i/dt$. To calculate $dP/dt$ we thus simply sum the rhs of Eq.1 over $i$, which gives zero.