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3 Master equation

This is the lecture note on May 7, 2024 introducing the master equation and detailed balance condition.

3.1 Basic formulation

We consider N distinct (classical) states where N could be infinite. We will discuss the transitions of a target system among these N states by the effect of the environment (typically in thermal equilibrium).

First we discretize the time with a step Δt. If one focuses on a state k, within this unit of time Δt, the system may jump to other states ℓ ($\neq k$) with a probability, $P_{\ell k}$ (≥ 0). Here, we restrict ourselves to a time-independent situations where $P_{\ell k}$ are some constants independent of time. It is important to note the order of the indexes of $P_{\ell k}$ for the process from k to ℓ. In general $P_{\ell k}$ could be different from $P_{k\ell}$. The sum $\sum_{\ell=1,\ell\neq k}^{N} P_{\ell k}$ needs not to be one. The rest, $1-\sum_{\ell=1,\ell\neq k}^{N} P_{\ell k}$, represents the probability of a state k be still within the time Δt.

We consider the probability distribution function, $W_k(n)$, representing that the system is in a state k at the time instance $t = n\Delta t$. The conditions for this probability distribution function are

$$W_k(n) \geq 0, \ \ \text{for } \forall k, n, \tag{1}$$

$$\sum_{k=1}^{N} W_k(n) = 1, \ \ \text{for } \forall n, \tag{2}$$

where the second condition is from probability conservation. The difference equation for $W_k(n)$, $n > 1$, is easily derived as

$$W_k(n) = \left(1 - \sum_{\ell=1,\ell\neq k}^{N} P_{\ell k}\right) W_k(n-1) + \sum_{\ell=1,\ell\neq k}^{N} P_{k,\ell} W_\ell(n-1). \tag{3}$$

The first term on the right is the decrease of the probability by the **scattering-out processes** and the second term represents the increase of the probability by the **scattering-in processes**.

Now we take the continuum limit by taking $\Delta t \to 0$ and the probability distribution function becomes $W_k(n) \to W_k(t) = W_k(n\Delta t)$. Assuming that the function $W_k(t)$ is differentiable, we expand it in a Taylor series,

$$W_k(t-\Delta t) = W_k(t) - \frac{\partial W_k(t)}{\partial t}\Delta t + o\left((\Delta t)^2\right). \tag{4}$$

By putting this to the right-hand-side of the difference equation, Eq. (3), up to order Δt,

$$\begin{aligned}\text{RHS} &= \left(1 - \sum_{\ell=1,\ell\neq k}^{N} P_{\ell k}\right)\left\{W_k(t) - \frac{\partial W_k(t)}{\partial t}\Delta t\right\} + \sum_{\ell=1,\ell\neq k}^{N} P_{k,\ell}\left\{W_\ell(t) - \frac{\partial W_\ell(t)}{\partial t}\Delta t\right\} \\ &= W_k(t) - \sum_{\ell=1,\ell\neq k}^{N} P_{\ell k}W_k(t) - \frac{\partial W_k(t)}{\partial t}\Delta t + \sum_{\ell=1,\ell\neq k}^{N} P_{k\ell}W_\ell(t) + \sum_{\ell=1,\ell\neq k}^{N}\left\{P_{\ell k}\frac{\partial W_k(t)}{\partial t} - P_{k\ell}\frac{\partial W_\ell(t)}{\partial t}\right\}\Delta t.\end{aligned} \tag{5}$$

Hence, arranging the equation, we have

$$\frac{\partial W_k(t)}{\partial t}\Delta t = \sum_{\ell=1,\ell\neq k}^{N} \left\{ -P_{\ell k}W_k(t) + P_{k\ell}W_\ell(t) + \left[P_{\ell k}\frac{\partial W_k(t)}{\partial t} - P_{k\ell}\frac{\partial W_\ell(t)}{\partial t} \right] \Delta t \right\}. \tag{6}$$

Assuming we have a well defined limit

$$\lim_{\Delta t\to 0} \frac{P_{\ell k}}{\Delta t} = \gamma_{\ell k}, \tag{7}$$

hence $P_{\ell k}$ itself is the order of Δt. This parameter $\gamma_{\ell k}$ is called a **transition rate** from a state k to ℓ. Then dividing Eq. (6) by Δt and taking the limit $\Delta t \to 0$, we have

$$\frac{\partial W_k(t)}{\partial t} = \gamma_{kk}W_k(t) + \sum_{\ell=1,\ell\neq k}^{N} \gamma_{k\ell}W_\ell(t), \tag{8}$$

where we introduced

$$\gamma_{kk} \equiv -\sum_{\ell=1,\ell\neq k}^{N} \gamma_{\ell k}. \tag{9}$$

Equation (8) is the (classical) **master equation**.

3.2 Vector notation and general properties of master equation

For the brevity of the presentation, we introduce a probability (ket) vector at time t,

$$|W(t)\rangle \equiv \begin{pmatrix} W_1(t) \\ W_2(t) \\ \vdots \\ W_N(t) \end{pmatrix}, \tag{10}$$

and we introduce a special bra vector

$$\langle 0| \equiv (1, 1, \ldots, 1), \tag{11}$$

where the number of elements is N. Then the property of the conservation of probability, Eq. (2), is

$$\langle 0|W(t)\rangle = 1, \quad \text{for } \forall t. \tag{12}$$

The master equation can be cast into the matrix form

$$\frac{\partial}{\partial t} |W(t)\rangle = \hat{M} |W(t)\rangle, \tag{13}$$

where the $N \times N$ matrix $\hat{M}$ is defined as

$$\hat{M} = \begin{pmatrix} \gamma_{11} & \gamma_{12} & \cdots & \gamma_{1N} \\ \gamma_{21} & \gamma_{22} & \cdots & \gamma_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \gamma_{N1} & \gamma_{N2} & \cdots & \gamma_{NN} \end{pmatrix}, \tag{14}$$

and all the off-diagonal elements are nonzero and the diagonal elements are negative. There is an important relation, from Eq. (9), for all k,

$$\sum_{\ell=1}^{N} \gamma_{\ell k} = 0, \tag{15}$$

which is equivalent to the relation

$$\langle 0| \hat{M} = (0, 0, \cdots, 0). \tag{16}$$

This relation can also be derived from the conservation of probability, Eq. (12),

$$0 = \frac{\partial}{\partial t} \langle 0|W(t)\rangle = \langle 0| \frac{\partial}{\partial t} |W(t)\rangle = \langle 0| \hat{M} |W(t)\rangle , \tag{17}$$

for any probability vector $|W(t)\rangle$, hence $\langle 0| \hat{M} = (0, 0, \cdots, 0)$. Since the real matrix $\hat{M}$ is not symmetric in general, the left and the right eigenvectors, defined by $\langle n| , |n\rangle$

$$\hat{M} |n\rangle = \lambda_n |n\rangle , \tag{18}$$
$$\langle n| \hat{M} = \lambda_n \langle n| , \tag{19}$$

for $n = 0, \ldots, N-1$ are not equivalent (not Hermite conjugate, $\langle n|^\dagger \neq |n\rangle$). Corresponding eigenvalues λ_n are in general complex numbers. The eigenvectors satisfy orthogonality and completeness relations,

$$\langle n|m\rangle = \delta_{nm}, \tag{20}$$
$$\sum_{n=0}^{N-1} |n\rangle \langle n| = \hat{1}, \tag{21}$$

where $\hat{1}$ is $N \times N$ identity matrix. It is known that all the real parts of the eigenvalue λ_n are non-positive. There is at least one zero eigenvalue and we assume it to be only one in the following discussions. We rearrange the eigenvalues in a descending order of their real parts. Hence, $\lambda_0 = 0$ and $|0\rangle , \langle 0|$ are corresponding right and left eigenvectors, respectively. In Eq. (16), $\langle 0|$ was already defined as a special bra-vector with eigenvalue zero, Eq. (16). Hence, $\langle 0|m\rangle = 0$ for $m \geq 1$ from the orthonormality condition Eq. (20).

Using the completeness property of the eigenvectors, we can expand the probability vector

$$|W(t)\rangle = \sum_{n=0}^{N-1} |n\rangle \langle n| |W(t)\rangle = \sum_{n=0}^{N-1} c_n(t) |n\rangle , \tag{22}$$

where $c_n(t) \equiv \langle n|W(t)\rangle$. Clearly, $c_0(t) = \langle 0|W(t)\rangle = 1$ for any t. By putting this into the master equation (13),

$$\frac{\partial}{\partial t} |W(t)\rangle = \sum_{n=0}^{N-1} \frac{\partial c_n(t)}{\partial t} |n\rangle = \hat{M} |W(t)\rangle = \sum_{n=0}^{N-1} c_n(t) \hat{M} |n\rangle = \sum_{n=0}^{N-1} c_n(t) \lambda_n |n\rangle , \tag{23}$$

and by applying $\langle m|$ from the left and using the orthogonality relation, we have

$$\frac{\partial c_m(t)}{\partial t} = \lambda_m c_m(t). \tag{24}$$

The general solution is

$$c_m(t) = e^{\lambda_m t} c_m(0), \tag{25}$$

where $c_m(0) = \langle m|W(0)\rangle$ is the initial value at $t = 0$. Hence, the dynamics of the state vector is solved as

$$\begin{aligned} |W(t)\rangle &= \sum_{n=0}^{N-1} e^{\lambda_n t} c_n(0) |n\rangle = \sum_{n=0}^{N-1} e^{\lambda_n t} |n\rangle \langle n|W(0)\rangle \\ &= e^{\hat{M} t} \sum_{n=0}^{N-1} |n\rangle \langle n|W(0)\rangle = e^{\hat{M} t} |W(0)\rangle , \end{aligned} \tag{26}$$

where the last equation is just the formal expression of the solution.

Using the property that the real part of λ_m is negative, for $m \geq 1$,

$$\lim_{t \to \infty} c_m(t) = 0, \tag{27}$$

from any initial condition $c_m(0)$. Hence, $|0\rangle \equiv |W_{\rm st}\rangle$ has also a special meaning of the **steady state** such that

$$\lim_{t\to\infty} |W(t)\rangle = \lim_{t\to\infty} \sum_{n=0}^{N-1} c_n(t) |n\rangle = \lim_{t\to\infty} c_0(t) |0\rangle = |0\rangle = |W_{\rm st}\rangle . \tag{28}$$

One should note that $|W_{\rm st}\rangle$ is determined from following two conditions:

$$\hat{M} |W_{\rm st}\rangle = 0, \quad \langle 0|W_{\rm st}\rangle = 1, \tag{29}$$

where $\langle 0|$ is defined in Eq. (11).

3.3 Detailed balance

The master equation can describe any non-equilibrium situations like heat flows as well as biological systems under certain choices of the transition rates. If the system is in contact with an environment in thermal equilibrium of temperature T, and the system states k represent energy eigenstate with energy E_k, the transition rates satisfy following **detailed balance condition**:

$$\frac{\gamma_{\ell k}}{\gamma_{k\ell}} = e^{\beta(E_k - E_\ell)}, \tag{30}$$

where $\beta = (k_{\rm B}T)^{-1}$ with the Boltzmann constant $k_{\rm B}$. [1] This is a **sufficient condition** that the focused system and the environment becomes an equilibrium at temperature T in the steady state (after a long time).

Let us show this physical picture using a simplest example of the dynamics with $N = 2$ given by the master equation. We consider two non-degenerated system states a and b with corresponding energies E_a and E_b, respectively. Without loss of generality, we assume $E_a < E_b$. The master equation is

$$\frac{dW_a(t)}{dt} = \gamma_{aa} W_a(t) + \gamma_{ab} W_b(t), \tag{31}$$

$$\frac{dW_b(t)}{dt} = \gamma_{bb} W_b(t) + \gamma_{ba} W_a(t), \tag{32}$$

where $\gamma_{aa} = -\gamma_{ba} \leq 0$ and $\gamma_{bb} = -\gamma_{ab} \leq 0$ (the case $\gamma_{ba} = 0$ and $\gamma_{ab} = 0$ induces two zero eigenstates, which is excluded in this discussion). Hence, the matrix $\hat{M}$ is

$$\hat{M} = \begin{pmatrix} -\gamma_{ba} & \gamma_{ab} \\ \gamma_{ba} & -\gamma_{ab} \end{pmatrix}. \tag{33}$$

The two eigenvalues of this matrix is 0 and $-(\gamma_{ab} + \gamma_{ba})$. The right-eigenvector corresponding to the eigenvalue 0 is

$$|0\rangle = C \begin{pmatrix} \gamma_{ab} \\ \gamma_{ba} \end{pmatrix}, \tag{34}$$

where the positive constant C is determined by the normalization condition, $1 = \langle 0|0\rangle = C(\gamma_{ab} + \gamma_{ba})$, hence the probability distribution of the steady state $|W_{\rm st}\rangle = |0\rangle$ is

$$|W_{\rm st}\rangle = \begin{pmatrix} \frac{\gamma_{ab}}{\gamma_{ab}+\gamma_{ba}} \\ \frac{\gamma_{ba}}{\gamma_{ab}+\gamma_{ba}} \end{pmatrix}. \tag{35}$$

[1] In this argument, we do not consider an exchange of particles between the system and the particle reservoir, which will be discussed in the next lecture.

When the system is in thermal equilibrium at inverse temperature β, these probabilities should be the Gibbs distribution, namely,

$$|W_{\rm st}\rangle \propto \begin{pmatrix} e^{-\beta E_a} \\ e^{-\beta E_b} \end{pmatrix}. \tag{36}$$

Hence, the ratio

$$\frac{\gamma_{ab}}{\gamma_{ba}} = e^{\beta(E_b - E_a)}, \tag{37}$$

obeys detailed balance condition. It is straightforward to extend the argument to more than two level systems.

If the system is in contact with more than one reservoirs with different temperatures, the notion of the detailed balance condition can be generalized, namely,

$$\frac{\gamma_{\ell k}^{(c)}}{\gamma_{k\ell}^{(c)}} = e^{\beta_c(E_k - E_\ell)}, \tag{38}$$

where $\gamma_{\ell k}^{(c)}$ represents the transition rate by the effect of only the reservoir c in thermal equilibrium of inverse temperature β_c. Such a separation of the transition processes to a particular reservoir may only be possible when the couplings to the reservoirs are weak enough or restricted to spatially localized couplings.

3.4 Conclusions

We have introduced the master equation and its basic properties, namely the existence of a steady state and detailed balance relation when it is coupled to a reservoir in thermal equilibrium.