

# Notes on the derivation of the Redfield equation

XuanLeng

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## 1 Redfield theory

(1) System model.

In condensed phase dynamics, one is typically interested in the detailed behavior of only a small part of the overall system and so one partitions the total system into the sub-system of interest and a bath (reservoir, environment), with the Hamiltonian

$$H_{tot} = H_S + H_B + H_{SB} = H_0 + H_{SB} \quad (1)$$

Here,  $H_S$  is the Hamiltonian of the isolated sub-system (henceforth called simply the system);  $H_B$  is the Hamiltonian of bath; and the two parts are combined as  $H_0 \equiv H_S + H_B$ .  $H_{SB}$  describes their interaction. The system-bath interaction can always, in principle, be written as a sum of products of separate system and bath operators, i.e.,

$$H_{SB} = \sum_n S_n \cdot B_n \quad (2)$$

where the  $S_n$  and  $B_n$  act only on functions of the system and bath variables, respectively.

(2) Second order expanding.

The density matrix of total system is  $\rho_{tot}(t)$ . Its time evolution equation is the Liouville-von Neumann equation

$$\frac{d}{dt}\rho_{tot}(t) = -\frac{i}{\hbar}[H, \rho_{tot}(t)] \quad (3)$$

All the information of the total system is contained in the equation. But we can not directly solve it, since the Hamiltonian of total system is infinity.

Go to the interaction picture (symbol ‘ $\sim$ ’). Then Liouville-von Neumann equation (Eq.3) becomes

$$\frac{d}{dt}\tilde{\rho}_{tot}(t) = -\frac{i}{\hbar}[\tilde{H}_{SB}(t), \tilde{\rho}_{tot}(t)] \quad (4)$$

where

$$\tilde{\rho}_{tot}(t) = U^{-1}(t)\rho_{tot}(t)U(t) = e^{\frac{i}{\hbar}H_0t}\rho_{tot}(t)e^{-\frac{i}{\hbar}H_0t} \quad (5)$$

$$\begin{aligned} \tilde{H}_{SB}(t) &= e^{\frac{i}{\hbar}H_0t}H_{SB}e^{-\frac{i}{\hbar}H_0t} = e^{\frac{i}{\hbar}(H_S+H_B)t}H_{SB}e^{-\frac{i}{\hbar}(H_S+H_B)t} \\ &= \sum_n e^{\frac{i}{\hbar}H_S t}S_n e^{-\frac{i}{\hbar}H_S t} e^{\frac{i}{\hbar}H_B t}B_n e^{-\frac{i}{\hbar}H_B t} = \sum_n \tilde{S}_n(t)\tilde{B}_n(t) \end{aligned} \quad (6)$$

$$\tilde{S}_n(t) = e^{\frac{i}{\hbar}H_S t}S_n e^{-\frac{i}{\hbar}H_S t} \quad (7)$$

$$\tilde{B}_n(t) = e^{\frac{i}{\hbar}H_B t}B_n e^{-\frac{i}{\hbar}H_B t} \quad (8)$$

Integrate both side of Eq.4 with arbitray start time  $t_0$ .

$$\int_{t_0}^t d\tilde{\rho}_{tot}(\tau) = -\frac{i}{\hbar} \int_{t_0}^t d\tau [\tilde{H}_{SB}(\tau), \tilde{\rho}_{tot}(\tau)] \quad (9)$$

$$\tilde{\rho}_{tot}(t) = \tilde{\rho}_{tot}(t_0) - \frac{i}{\hbar} \int_{t_0}^t d\tau [\tilde{H}_{SB}(\tau), \tilde{\rho}_{tot}(\tau)] \quad (10)$$

Insert the Eq.10 back to the right side of Eq.4. Then we get

$$\frac{d}{dt}\tilde{\rho}_{tot}(t) = -\frac{i}{\hbar} \left[ \tilde{H}_{SB}(t), \tilde{\rho}_{tot}(t_0) - \frac{i}{\hbar} \int_{t_0}^t d\tau [\tilde{H}_{SB}(\tau), \tilde{\rho}_{tot}(\tau)] \right] \quad (11)$$

$$\frac{d}{dt}\tilde{\rho}_{tot}(t) = -\frac{i}{\hbar} [\tilde{H}_{SB}(t), \tilde{\rho}_{tot}(t_0)] - \frac{1}{\hbar^2} \int_{t_0}^t d\tau [\tilde{H}_{SB}(t), [\tilde{H}_{SB}(\tau), \tilde{\rho}_{tot}(\tau)]] \quad (12)$$

Currently, we have not do any approximation. The equation is exact.

(3) Trace the bath.

Trace over the bath, we will get the reduced system density matrix  $\tilde{\rho}_S(t)$ ,

$$\begin{aligned} \text{Tr}_B[\tilde{\rho}_{tot}(t)] &= \text{Tr}_B \left[ e^{\frac{i}{\hbar}H_0t}\rho_{tot}(t)e^{-\frac{i}{\hbar}H_0t} \right] = e^{\frac{i}{\hbar}H_S t} \text{Tr}_B \left[ e^{\frac{i}{\hbar}H_B t}\rho_{tot}(t)e^{-\frac{i}{\hbar}H_B t} \right] e^{-\frac{i}{\hbar}H_S t} \\ &= e^{\frac{i}{\hbar}H_S t} \text{Tr}_B \left[ e^{-\frac{i}{\hbar}H_B t} e^{\frac{i}{\hbar}H_B t} \rho_{tot}(t) \right] e^{-\frac{i}{\hbar}H_S t} \\ &= e^{\frac{i}{\hbar}H_S t} \text{Tr}_B [\rho_{tot}(t)] e^{-\frac{i}{\hbar}H_S t} \\ &= e^{\frac{i}{\hbar}H_S t} \rho_S(t) e^{-\frac{i}{\hbar}H_S t} \\ &= \tilde{\rho}_S(t) \end{aligned} \quad (13)$$

Then we get

$$\frac{d}{dt}\tilde{\rho}_S(t) = -\frac{i}{\hbar} \text{Tr}_B \left\{ [\tilde{H}_{SB}(t), \tilde{\rho}_{tot}(t_0)] \right\} - \frac{1}{\hbar^2} \int_{t_0}^t d\tau \text{Tr}_B \left\{ [\tilde{H}_{SB}(t), [\tilde{H}_{SB}(\tau), \tilde{\rho}_{tot}(\tau)]] \right\} \quad (14)$$

(4.1) Initial state assumption.(Ref.[3])

Assume that at time  $t_0 = 0$  the pigment system and bath are in a separable state

$$\rho_{tot}(0) = \rho_S(0) \otimes \rho_B(0) \quad (15)$$

this can always be obtained by choosing  $t_0 = 0$  appropriately. Then the second term in the RHS of Eq.12 becomes

$$\text{Tr}_B \left\{ [\tilde{H}_{SB}(t), \tilde{\rho}_{tot}(0)] \right\} = \sum_n [\tilde{S}_n(t), \tilde{\rho}_S(0)] \text{Tr}_B [\tilde{B}_n(t) \rho_B(0)] \quad (16)$$

that is, we consider the expectation value of the operators  $B_n$ . In general we will also need to take an ensemble average over the random fluctuating field  $\langle B_n(t) \rangle$ , as we look at expectation values for the density operator. We can now make the assumption that  $\langle B_n \rangle_B = 0$ , , which implies  $\text{Tr}_B [\tilde{H}_{SB}(t) \rho_B(0)] = 0$ . This is not restrictive, since, if  $H_{SB}$  is of the form  $H_{SB} = S \otimes B$  with  $\langle B \rangle \neq 0$  we can replace  $H_{SB}$  with  $H_{SB} = S \otimes (B - \langle B \rangle_B)$ , and simultaneously add  $S \langle B \rangle_B$  to  $H_S$ . With this condition,  $\langle H_{SB} \rangle_B = 0$  and since  $\rho_B(0)$  has the same form in both Schrödinger and interaction pictures, the result holds in the interaction picture also. The same argument can be made if  $H_{SB} = \sum_n S_n \otimes B_n$ . Then the second term in the Eq.12 vanishes and we have

$$\frac{d}{dt} \tilde{\rho}_S(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ [\tilde{H}_{SB}(t), [\tilde{H}_{SB}(\tau), \tilde{\rho}_{tot}(\tau)]] \right\} \quad (17)$$

This equation can not be solved, we need make some approximations.

(4.2) Born approximation.(Ref.[3])

Assume that the coupling between the system and the bath is weak and the bath is always in a thermal equilibrium.

$$\rho_{tot}(t) = \rho_S(t) \otimes \rho_B(0) \quad (18)$$

$$\rho_B(0) = \frac{e^{-\beta H_B}}{Z} \quad (19)$$

where  $\beta = 1/K_B T$ ,  $[\rho_B(0), H_B] = 0$  which is a stationary state.  $\rho_B(0)$  has the same form in both the interaction picture and Schrödinger picture.

(4.3) Markov approximation.(Ref.[3])

We will also assume that we are working over timescales that are shorter than the gross timescale over which the system evolves, so that

$$\tilde{\rho}_S(\tau) = \tilde{\rho}_S(t) \quad (20)$$

Then Eq.17 becomes

$$\frac{d}{dt} \tilde{\rho}_S(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ [\tilde{H}_{SB}(t), [\tilde{H}_{SB}(\tau), \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)]] \right\} \quad (21)$$

(5) Change the integration variable.

Set  $\tau' = t - \tau$ , then  $\tau = t - \tau'$ . We have

$$\int_0^t d\tau = \int_t^0 d(t - \tau') = - \int_t^0 d\tau' = \int_0^t d\tau' \quad (22)$$

Then

$$\frac{d}{dt}\tilde{\rho}_S(t) = -\frac{1}{\hbar^2} \int_0^t d\tau' \text{Tr}_B \left\{ \left[ \tilde{H}_{SB}(t), [\tilde{H}_{SB}(t-\tau'), \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)] \right] \right\} \quad (23)$$

Rewrite  $\tau'$  to  $\tau$ , we have

$$\frac{d}{dt}\tilde{\rho}_S(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \left[ \tilde{H}_{SB}(t), [\tilde{H}_{SB}(t-\tau), \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)] \right] \right\} \quad (24)$$

(6) Expanding the equation.

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}_S(t) &= -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \left[ \tilde{H}_{SB}(t), [\tilde{H}_{SB}(t-\tau)\tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0) - \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)\tilde{H}_{SB}(t-\tau)] \right] \right\} \\ &= -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \tilde{H}_{SB}(t)\tilde{H}_{SB}(t-\tau)\tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0) \right. \\ &\quad - \tilde{H}_{SB}(t-\tau)\tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)\tilde{H}_{SB}(t) \\ &\quad - \tilde{H}_{SB}(t)\tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)\tilde{H}_{SB}(t-\tau) \\ &\quad \left. + \tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)\tilde{H}_{SB}(t-\tau)\tilde{H}_{SB}(t) \right\} \end{aligned} \quad (25)$$

where

$$\begin{aligned} \text{Tr}_B \left[ \tilde{H}_{SB}(t)\tilde{H}_{SB}(t-\tau)\tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0) \right] &= \sum_{m,n} \text{Tr}_B \left[ \tilde{S}_m(t)\tilde{B}_m(t)\tilde{S}_n(t-\tau)\tilde{B}_n(t-\tau)\tilde{\rho}_S(t)\tilde{\rho}_B(0) \right] \\ &= \sum_{m,n} \text{Tr}_B \left[ \tilde{B}_m(t)\tilde{B}_n(t-\tau)\tilde{\rho}_B(0) \right] \tilde{S}_m(t)\tilde{S}_n(t-\tau)\tilde{\rho}_S(t) \\ &= \sum_{m,n} \left\langle \tilde{B}_m(t)\tilde{B}_n(t-\tau) \right\rangle_B \tilde{S}_m(t)\tilde{S}_n(t-\tau)\tilde{\rho}_S(t) \end{aligned} \quad (26)$$

$$\begin{aligned} \text{Tr}_B \left[ \tilde{H}_{SB}(t-\tau)\tilde{\rho}_S(t) \otimes \tilde{\rho}_B(0)\tilde{H}_{SB}(t) \right] &= \sum_{m,n} \text{Tr}_B \left[ \tilde{S}_n(t-\tau)\tilde{B}_n(t-\tau)\tilde{\rho}_S(t)\tilde{\rho}_B(0)\tilde{S}_m(t)\tilde{B}_m(t) \right] \\ &= \sum_{m,n} \text{Tr}_B \left[ \tilde{B}_n(t-\tau)\tilde{\rho}_B(0)\tilde{B}_m(t) \right] \tilde{S}_n(t-\tau)\tilde{\rho}_S(t)\tilde{S}_m(t) \\ &= \sum_{m,n} \text{Tr}_B \left[ \tilde{B}_m(t)\tilde{B}_n(t-\tau)\tilde{\rho}_B(0) \right] \tilde{S}_n(t-\tau)\tilde{\rho}_S(t)\tilde{S}_m(t) \\ &= \sum_{m,n} \left\langle \tilde{B}_m(t)\tilde{B}_n(t-\tau) \right\rangle_B \tilde{S}_n(t-\tau)\tilde{\rho}_S(t)\tilde{S}_m(t) \end{aligned} \quad (27)$$

here

$$\left\langle \tilde{B}_m(t)\tilde{B}_n(t-\tau) \right\rangle = \text{tr}_B \left[ \tilde{B}_m(t)\tilde{B}_n(t-\tau)\rho_B(0) \right] \quad (28)$$

is the bath correlation function. Rewrite it as

$$\begin{aligned} \left\langle \tilde{B}_m(t)\tilde{B}_n(t-\tau) \right\rangle &= \text{tr}_B \left[ \tilde{B}_m(t)\tilde{B}_n(t-\tau)\rho_B(0) \right] \\ &= \text{tr}_B \left[ e^{\frac{i}{\hbar}H_B t} B_m(0) e^{-\frac{i}{\hbar}H_B t} e^{\frac{i}{\hbar}H_B(t-\tau)} B_n(0) e^{-\frac{i}{\hbar}H_B(t-\tau)} \cdot \rho_B(0) \right] \\ &= \text{tr}_B \left[ e^{-\frac{i}{\hbar}H_B(t-\tau)} e^{\frac{i}{\hbar}H_B t} B_m(0) e^{-\frac{i}{\hbar}H_B t} e^{\frac{i}{\hbar}H_B(t-\tau)} B_n(0) \cdot \rho_B(0) \right] \\ &= \text{tr}_B \left[ e^{\frac{i}{\hbar}H_B \tau} B_m(0) e^{-\frac{i}{\hbar}H_B \tau} B_n(0) \cdot \rho_B(0) \right] \\ &= \left\langle \tilde{B}_m(\tau)\tilde{B}_n(0) \right\rangle \end{aligned}$$

$$\begin{aligned}
&= \text{tr}_B \left[ B_m(0) e^{-\frac{i}{\hbar} H_B t} e^{\frac{i}{\hbar} H_B (t-\tau)} B_n(0) e^{-\frac{i}{\hbar} H_B (t-\tau)} e^{\frac{i}{\hbar} H_B t} \cdot \rho_B(0) \right] \\
&= \left\langle \tilde{B}_m(0) \tilde{B}_n(-\tau) \right\rangle
\end{aligned} \tag{29}$$

After the correlation time  $\tau_c$ , the correlation function becomes 0. So we can therefore extend the limit of integration to  $+\infty$ . Then

$$\begin{aligned}
\frac{d}{dt} \tilde{\rho}_S(t) &= -\frac{1}{\hbar^2} \int_0^\infty d\tau \sum_{m,n} \left\{ \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B \tilde{S}_m(t) \tilde{S}_n(t-\tau) \tilde{\rho}_S(t) \right. \\
&\quad - \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B \tilde{S}_n(t-\tau) \tilde{\rho}_S(t) \tilde{S}_m(t) \\
&\quad - \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B \tilde{S}_m(t) \tilde{\rho}_S(t) \tilde{S}_n(t-\tau) \\
&\quad \left. + \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B \tilde{\rho}_S(t) \tilde{S}_n(t-\tau) \tilde{S}_m(t) \right\}
\end{aligned} \tag{30}$$

(7) Back to Schrödinger picture.

$$\tilde{\rho}_S(t) = e^{\frac{i}{\hbar} H_S t} \rho_S(t) e^{-\frac{i}{\hbar} H_S t} \implies \tag{31}$$

$$\begin{aligned}
\frac{d}{dt} \tilde{\rho}_S(t) &= \frac{i}{\hbar} H_S e^{\frac{i}{\hbar} H_S t} \rho_S(t) e^{-\frac{i}{\hbar} H_S t} + e^{\frac{i}{\hbar} H_S t} \left[ \frac{d}{dt} \rho_S(t) \right] e^{-\frac{i}{\hbar} H_S t} - e^{\frac{i}{\hbar} H_S t} \rho_S(t) \frac{i}{\hbar} H_S e^{-\frac{i}{\hbar} H_S t} \\
&= e^{\frac{i}{\hbar} H_S t} \left[ \frac{d}{dt} \rho_S(t) \right] e^{-\frac{i}{\hbar} H_S t} - \frac{i}{\hbar} e^{\frac{i}{\hbar} H_S t} [\rho_S(t), H_S] e^{-\frac{i}{\hbar} H_S t}
\end{aligned} \tag{32}$$

Put above equations into Eq.30, we have

$$\begin{aligned}
\frac{d}{dt} \rho_S(t) - \frac{i}{\hbar} [\rho_S(t), H_S] &= -\frac{1}{\hbar^2} \int_0^\infty d\tau \sum_{m,n} \left\{ \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B e^{-\frac{i}{\hbar} H_S t} \tilde{S}_m(t) \tilde{S}_n(t-\tau) \tilde{\rho}_S(t) e^{\frac{i}{\hbar} H_S t} \right. \\
&\quad - \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B e^{-\frac{i}{\hbar} H_S t} \tilde{S}_n(t-\tau) \tilde{\rho}_S(t) \tilde{S}_m(t) e^{\frac{i}{\hbar} H_S t} \\
&\quad - \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B e^{-\frac{i}{\hbar} H_S t} \tilde{S}_m(t) \tilde{\rho}_S(t) \tilde{S}_n(t-\tau) e^{\frac{i}{\hbar} H_S t} \\
&\quad \left. + \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B e^{-\frac{i}{\hbar} H_S t} \tilde{\rho}_S(t) \tilde{S}_n(t-\tau) \tilde{S}_m(t) e^{\frac{i}{\hbar} H_S t} \right\}
\end{aligned} \tag{33}$$

Since

$$\begin{aligned}
&e^{-\frac{i}{\hbar} H_S t} \tilde{S}_m(t) \tilde{S}_n(t-\tau) \tilde{\rho}_S(t) e^{\frac{i}{\hbar} H_S t} \\
&= e^{-\frac{i}{\hbar} H_S t} e^{\frac{i}{\hbar} H_S t} S_m(0) e^{-\frac{i}{\hbar} H_S t} e^{\frac{i}{\hbar} H_S (t-\tau)} S_n(0) e^{-\frac{i}{\hbar} H_S (t-\tau)} e^{\frac{i}{\hbar} H_S t} \rho_S(t) e^{-\frac{i}{\hbar} H_S t} e^{\frac{i}{\hbar} H_S t} \\
&= S_m(0) e^{\frac{i}{\hbar} H_S (-\tau)} S_n(0) e^{-\frac{i}{\hbar} H_S (-\tau)} \rho_S(t) \\
&= \tilde{S}_m(0) \tilde{S}_n(-\tau) \rho_S(t)
\end{aligned} \tag{34}$$

we get

$$\begin{aligned}
\frac{d}{dt} \rho_S(t) - \frac{i}{\hbar} [\rho_S(t), H_S] &= -\frac{1}{\hbar^2} \int_0^\infty d\tau \sum_{m,n} \left\{ \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B \tilde{S}_m(0) \tilde{S}_n(-\tau) \rho_S(t) \right. \\
&\quad - \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B \tilde{S}_n(-\tau) \rho_S(t) \tilde{S}_m(0) \\
&\quad - \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B \tilde{S}_m(0) \rho_S(t) \tilde{S}_n(-\tau) \\
&\quad \left. + \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B \rho_S(t) \tilde{S}_n(-\tau) \tilde{S}_m(0) \right\}
\end{aligned} \tag{35}$$

(8) Switch to the eigenstate representation of  $H_S$ .

There are two possibilities to represent the reduced density operator  $\rho_S(t)$ . First, one can choose a site representation in terms of the  $\{|n\rangle\}$  basis, which gives the reduced density matrix  $\rho_S^{site}(t)_{mn} \equiv \langle m|\rho_S(t)|n\rangle$ . On the other hand, the alternative to the site representation is provided by an eigenstate representation of the excitons  $\{|\nu\rangle\}$ . This gives a reduced density matrix such as  $\rho_S^{exc}(t)_{\mu\nu} \equiv \langle \mu|\rho_S(t)|\nu\rangle$ . In order to obtain exciton energies  $\{\epsilon_\nu\}$  and states  $\{|\nu\rangle\}$ , the system Hamiltonian is diagonalized by orthogonal matrix  $U$  via

$$U^{-1}H_S U = \Omega \quad (36)$$

where the  $\nu$ th diagonal element of  $\Omega$  is identical to the  $\nu$ th eigenenergy  $\epsilon_\nu$ . An exciton ket state can be expanded as

$$|\nu\rangle = \sum_n (U^{-1})_{\nu n} |n\rangle = \sum_n U_{n\nu}^* |n\rangle \quad (37)$$

Hence, the two representations of the reduced density operator are transformed to each other as follows

$$U^{-1}\rho^{site}U = \rho^{exc} \quad (38)$$

Set

$$\omega_{\mu\nu} = (\epsilon_\mu - \epsilon_\nu)/\hbar \quad (39)$$

we have

$$\langle \mu|\rho_S(t)|\nu\rangle = \rho_S^{exc}(t)_{\mu\nu} \quad (40)$$

$$\begin{aligned} -\frac{i}{\hbar}\langle \mu|[\rho_S(t), H_S]|\nu\rangle &= \frac{i}{\hbar}[\langle \mu|H_S\rho_S(t)|\nu\rangle - \langle \mu|\rho_S(t)H_S|\nu\rangle] \\ &= \frac{i}{\hbar}[\epsilon_\mu\rho_S^{exc}(t)_{\mu\nu} - \epsilon_\nu\rho_S^{exc}(t)_{\mu\nu}] \\ &= i\omega_{\mu\nu}\rho_S^{exc}(t)_{\mu\nu} \end{aligned} \quad (41)$$

$$\begin{aligned} \langle \mu|\tilde{S}_m(0)\tilde{S}_n(-\tau)\rho_S(t)|\nu\rangle &= \sum_{\kappa,\mu'} \langle \mu|S_m|\kappa\rangle \langle \kappa|e^{-\frac{i}{\hbar}H_S\tau}S_n e^{\frac{i}{\hbar}H_S\tau}|\mu'\rangle \langle \mu'|\rho_S(t)|\nu\rangle \\ &= \sum_{\kappa,\mu'} (S_m)_{\mu\kappa} (S_n)_{\kappa\mu'} e^{-i\omega_{\kappa\mu'}\tau} \rho_S^{exc}(t)_{\mu'\nu} \\ &= \sum_{\nu'} \delta_{\nu'\nu} \sum_{\kappa,\mu'} (S_m)_{\mu\kappa} (S_n)_{\kappa\mu'} e^{-i\omega_{\kappa\mu'}\tau} \rho_S^{exc}(t)_{\mu'\nu'} \end{aligned} \quad (42)$$

$$\begin{aligned} \langle \mu|\tilde{S}_n(-\tau)\rho_S(t)\tilde{S}_m(0)|\nu\rangle &= \sum_{\mu',\nu'} \langle \mu|e^{-\frac{i}{\hbar}H_S\tau}S_n e^{\frac{i}{\hbar}H_S\tau}|\mu'\rangle \langle \mu'|\rho_S(t)|\nu'\rangle \langle \nu'|S_m|\nu\rangle \\ &= \sum_{\mu',\nu'} (S_n)_{\mu\mu'} (S_m)_{\nu'\nu} e^{-i\omega_{\mu\mu'}\tau} \rho_S^{exc}(t)_{\mu'\nu'} \end{aligned} \quad (43)$$

$$\begin{aligned} \langle \mu|\tilde{S}_m(0)\rho_S(t)\tilde{S}_n(-\tau)|\nu\rangle &= \sum_{\mu',\nu'} \langle \mu|S_m|\mu'\rangle \langle \mu'|\rho_S(t)|\nu'\rangle \langle \nu'|e^{-\frac{i}{\hbar}H_S\tau}S_n e^{\frac{i}{\hbar}H_S\tau}|\nu\rangle \\ &= \sum_{\mu',\nu'} (S_m)_{\mu\mu'} (S_n)_{\nu'\nu} e^{-i\omega_{\nu'\nu}\tau} \rho_S^{exc}(t)_{\mu'\nu'} \end{aligned} \quad (44)$$

$$\begin{aligned} \langle \mu|\rho_S(t)\tilde{S}_n(-\tau)\tilde{S}_m(0)|\nu\rangle &= \sum_{\nu',\kappa} \langle \mu|\rho_S(t)|\nu'\rangle \langle \nu'|e^{-\frac{i}{\hbar}H_S\tau}S_n e^{\frac{i}{\hbar}H_S\tau}|\kappa\rangle \langle \kappa|S_m|\nu\rangle \\ &= \sum_{\nu',\kappa} (S_n)_{\nu'\kappa} (S_m)_{\kappa\nu} e^{-i\omega_{\nu'\kappa}\tau} \rho_S^{exc}(t)_{\mu\nu'} \end{aligned}$$

$$= \sum_{\mu'} \delta_{\mu'\mu} \sum_{\nu', \kappa} (S_n)_{\nu'\kappa} (S_m)_{\kappa\nu} e^{-i\omega_{\nu'\kappa}} \rho_S^{exc}(t)_{\mu'\nu'} \quad (45)$$

For convenience, we will remove the subscript  $S$  of  $\rho_S^{exc}(t)$  and put Eq.40~ Eq.45 in Eq.35.

Then, we have

$$\begin{aligned} \frac{d}{dt} \rho_{\mu\nu}^{exc}(t) + i\omega_{\mu\nu} \rho_{\mu\nu}^{exc} = & - \sum_{\mu'\nu'} \left[ \delta_{\nu'\nu} \sum_{\kappa} \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B e^{-i\omega_{\kappa\mu'}\tau} (S_m)_{\mu\kappa} (S_n)_{\kappa\mu'} \right. \\ & - \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B e^{-i\omega_{\mu\mu'}\tau} (S_m)_{\nu'\nu} (S_n)_{\mu\mu'} \\ & - \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B e^{-i\omega_{\nu'\nu}\tau} (S_n)_{\nu'\nu} (S_m)_{\mu\mu'} \\ & \left. + \delta_{\mu'\mu} \sum_{\kappa} \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B e^{-i\omega_{\nu'\kappa}} (S_n)_{\nu'\kappa} (S_m)_{\kappa\nu} \right] \rho_{\mu'\nu'}^{exc}(t) \end{aligned} \quad (46)$$

(9) General form of Redfiled equation.

Set

$$\Gamma_{\nu'\nu\mu\mu'}^{(+)} = \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B e^{-i\omega_{\mu\mu'}\tau} (S_m)_{\nu'\nu} (S_n)_{\mu\mu'} \quad (47)$$

$$\Gamma_{\nu'\nu\mu\mu'}^{(-)} = \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B e^{-i\omega_{\nu'\nu}\tau} (S_n)_{\nu'\nu} (S_m)_{\mu\mu'} \quad (48)$$

$$R_{\mu\nu\mu'\nu'} = \Gamma_{\nu'\nu\mu\mu'}^{(+)} + \Gamma_{\nu'\nu\mu\mu'}^{(-)} - \delta_{\nu'\nu} \sum_{\kappa} \Gamma_{\mu\kappa\kappa\mu'}^{(+)} - \delta_{\mu'\mu} \sum_{\kappa} \Gamma_{\nu'\kappa\kappa\nu}^{(-)} \quad (49)$$

we have

$$\frac{d}{dt} \rho_{\mu\nu}^{exc}(t) = -i\omega_{\mu\nu} \rho_{\mu\nu}^{exc}(t) + \sum_{\mu'\nu'} R_{\mu\nu\mu'\nu'} \rho_{\mu'\nu'}^{exc}(t) \quad (50)$$

This is the most general form of Redfield equation.

(10) More compact form.

Considering

$$\begin{aligned} \Gamma_{\nu'\nu\mu\mu'}^{(-)*} &= \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B^* e^{i\omega_{\nu'\nu}\tau} (S_n)_{\nu'\nu}^* (S_m)_{\mu\mu'}^* \\ &= \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B e^{-i\omega_{\nu\nu'}\tau} (S_m)_{\mu'\mu} (S_n)_{\nu\nu'} \\ &= \Gamma_{\mu'\mu\nu\nu'}^{(+)} \end{aligned} \quad (51)$$

where

$$\left\langle \tilde{B}_n(0) \tilde{B}_m(\tau) \right\rangle_B^* = \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B \quad (52)$$

then, we get

$$\Gamma_{\nu'\nu\mu\mu'}^{(-)} = \Gamma_{\mu'\mu\nu\nu'}^{(+)*} \quad (53)$$

So the Redfield equation can written as

$$\frac{d}{dt}\rho_{\mu\nu}^{exc}(t) = -i\omega_{\mu\nu}\rho_{\mu\nu}^{exc}(t) + \sum_{\mu'\nu'} R_{\mu\nu\mu'\nu'}\rho_{\mu'\nu'}^{exc}(t) \quad (54)$$

where

$$R_{\mu\nu\mu'\nu'} = \Gamma_{\nu'\nu\mu\mu'} + \Gamma_{\mu'\mu\nu\nu'}^* - \delta_{\nu'\nu} \sum_{\kappa} \Gamma_{\mu\kappa\kappa\mu'} - \delta_{\mu'\mu} \sum_{\kappa} \Gamma_{\nu\kappa\kappa\nu'}^* \quad (55)$$

$$\Gamma_{\mu\nu\mu'\nu'} = \frac{1}{\hbar^2} \sum_{m,n} \int_0^\infty d\tau \langle \tilde{B}_m(\tau) \tilde{B}_n(0) \rangle_B e^{i\omega_{\nu'\mu'}\tau} (S_m)_{\mu\nu} (S_n)_{\mu'\nu'} \quad (56)$$

Should be noticed that the subscripts in Eq.55 and Eq.56 are independent. Don't get confused.

## 2 Bath correaltion functions and spectral density

Introducing a spectral distribution function of the electron-phonon coupling constants,  $J_{mn}(\omega)$ , one can express the correlation function as(Ref.[1])

$$C_{mn}(t) = \langle \tilde{B}_m(\tau) \tilde{B}_n(0) \rangle_B = \frac{\hbar}{\pi} \int_{-\infty}^{\infty} d\omega J_{mn}(\omega) [n_{BE}(\omega) + 1] e^{-i\omega t} \quad (57)$$

where

$$n_{BE}(\omega) \equiv \frac{1}{e^{\beta\hbar\omega} - 1} \quad (58)$$

is the Bose-Einstein distribution function<sup>1</sup> and we postulated the antisymmetry,

$$J_{mn}(-\omega) = -J_{nm}(\omega) \quad (62)$$

The absolute magnitude of the spectral distribution function is related to the reorganization energy by

$$\lambda_n = \int_0^\infty d\omega \frac{J_{nn}(\omega)}{\pi\omega} \quad (63)$$

Bath correlation function (Eq.57) can be simplified. Considering

$$\frac{1}{e^{\beta\hbar\omega} - 1} + 1 = \frac{1}{2} \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \quad e^{-i\omega t} = \cos \omega t - i \sin \omega t \quad (64)$$

<sup>1</sup> There are many forms, such as

$$\frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{e^{\beta\hbar\omega} - 1 + 1}{e^{\beta\hbar\omega} - 1} = \frac{1}{e^{\beta\hbar\omega} - 1} + 1 \quad (59)$$

$$\coth\left(\frac{\beta\hbar\omega}{2}\right) = 1 + \frac{2}{e^{\beta\hbar\omega} - 1} = 1 - \frac{2}{1 - e^{\beta\hbar\omega}} = 1 + \frac{2e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \quad (60)$$

Laurent expansion expression

$$\frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2} + \frac{1}{\beta\hbar\omega} + \frac{2}{\beta\hbar} \sum_{k=1}^{\infty} \frac{\omega}{\omega^2 + \nu_k^2} \quad (61)$$

here  $\nu_k = \frac{2\pi k}{\beta\hbar}$  is Matsubara frequency.

The real part of the bath correlation function becomes

$$\begin{aligned}
& \text{Re}C_{mn}(t) \\
&= \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t \\
&= \frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t + \frac{\hbar}{2\pi} \int_{-\infty}^0 d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t \\
&= \frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t - \frac{\hbar}{2\pi} \int_0^{-\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t \\
&= \frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t - \frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ -\coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \cos \omega t \\
&= \frac{\hbar}{\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) \cos \omega t \tag{65}
\end{aligned}$$

The image part of the bath correlation function becomes

$$\begin{aligned}
& \text{Im}C_{mn}(t) \\
&= -\frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t \\
&= -\frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t - \frac{\hbar}{2\pi} \int_{-\infty}^0 d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t \\
&= -\frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t + \frac{\hbar}{2\pi} \int_0^{-\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t \\
&= -\frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t - \frac{\hbar}{2\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ -\coth\left(\frac{\beta\hbar\omega}{2}\right) + 1 \right] \sin \omega t \\
&= -\frac{\hbar}{\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \sin \omega t \tag{66}
\end{aligned}$$

Then, we get

$$C_{mn}(t) = \left\langle \tilde{B}_m(\tau) \tilde{B}_n(0) \right\rangle_B = \frac{\hbar}{\pi} \int_0^{\infty} d\omega J_{mn}(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) \cos \omega t - i \sin \omega t \right] \tag{67}$$

The Fourier transform of the bath correlation function is

$$C_{mn}[\omega] \equiv \int_0^{\infty} dt e^{i\omega t} C_{mn}(t) \tag{68}$$

whose real and imaginary parts are expressed as

$$\text{Re}C_{mn}[\omega] = \hbar J_{mn}(\omega) [n_{BE}(\omega) + 1] \tag{69}$$

$$\text{Im}C_{mn}[\omega] = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\text{Re}C_{mn}[\omega']}{\omega - \omega'} \tag{70}$$

respectively. The symbol “ $P$ ” denotes the principal value of the integral.<sup>2</sup>

Then the Eq.56 can be expressed as

$$\Gamma_{abcd} = \frac{1}{\hbar^2} \sum_{m,n} C_{mn}[\omega_{dc}] (S_m)_{ab} (S_n)_{cd} \tag{71}$$

<sup>2</sup>refer to the Kramers-Kronig relations ( $k - k$  relations)

### 3 The photosynthetic light-harvesting system

We employ the following Frenkel exciton Hamiltonian to study excitation energy transfer (EET) dynamics of photosynthetic light-harvesting system,

$$H_{tot} = H_{el} + H_{ph} + H_{reorg} + H_{el-ph} \quad (72)$$

where

$$H_{el} = \sum_{n=1}^N |n\rangle\langle n| \epsilon_n^0 + \sum_{m<n} J_{mn} (|m\rangle\langle n| + |n\rangle\langle m|) \quad (73)$$

$$H_{ph} = \sum_{n=1}^N H_n^{ph}, \quad H_n^{ph} \equiv \sum_{\xi} \hbar\omega_{\xi} (p_{\xi}^2 + q_{\xi}^2)/2 \quad (74)$$

$$H_{reorg} = \sum_{n=1}^N |n\rangle\langle n| \lambda_n, \quad \lambda_n \equiv \sum_{\xi} \hbar\omega_{\xi} d_{n\xi}^2/2 \quad (75)$$

$$H_{el-ph} = \sum_{n=1}^N H_n^{el-ph} = \sum_{n=1}^N S_n B_n, \quad S_n = |n\rangle\langle n|, \quad B_n = - \sum_{\xi} \hbar\omega_{\xi} d_{n\xi} q_{\xi} \quad (76)$$

In the above

- $|n\rangle$  represents the state where only the  $n$ th site is in its excited electronic state  $|\varphi_{ne}\rangle$  and all others are in their ground electronic states  $|\varphi_{mg}\rangle$  that is

$$|n\rangle \equiv |\varphi_{ne}\rangle \prod_{n \neq m} |\varphi_{mg}\rangle \quad (77)$$

- $\epsilon_n^0$  is the excited electronic energy of the  $n$ th site in the absence of phonons.
- $J_{mn}$  is the electronic coupling Hamiltonian between the  $n$ th and  $m$ th sites, which is responsible for EET between the individual sites.
- $H_n^{ph}$  is the phonon Hamiltonian associated with the  $n$ th sites, where  $q_{\xi}$ ,  $p_{\xi}$ , and  $\omega_{\xi}$  are the dimensionless coordinate, conjugate momentum, and frequency of the  $\xi$ th phonon mode, respectively.
- $\lambda_n$  is the reorganization energy of the  $n$ th site, where  $d_{n\xi}$  is the dimensionless displacement of the equilibrium configuration of the  $\xi$ th phonon mode between the ground and excited electronic is the coupling states of the  $n$ th site.
- $H_n^{el-ph}$  is the coupling Hamiltonian between the  $n$ th site and phonon modes.

For simplicity, we assume that the phonon modes associated with one site are uncorrelated with those of another site.

$$C_{mn} \equiv \delta_{mn} C_n(t), \quad J_{mn} \equiv \delta_{mn} J_n(\omega) \quad (78)$$

Moreover, we assume that the phonon spectral distribution functions for each pigment are equivalent. Then, we have

$$C_{mn} \equiv \delta_{mn} C(t), \quad J_{mn} \equiv \delta_{mn} J(\omega) \quad (79)$$

and we employ the Drude—Lorentz density (the overdamped Brownian oscillator model)

$$J(\omega) = 2\lambda \frac{\omega\gamma}{\omega^2 + \gamma^2} \quad (80)$$

Considering Eq.76 and Eq.37

$$S_n = |n\rangle\langle n|$$

$$|\nu\rangle = \sum_n (U^{-1})_{\nu n} |n\rangle = \sum_n U_{n\nu}^* |n\rangle$$

we have

$$(S_n)_{ab} = \langle a|n\rangle\langle n|b\rangle = \langle n|a\rangle^* \langle n|b\rangle = U_{na} U_{nb}^* \quad (81)$$

$$(S_n)_{cd} = U_{nc} U_{nd}^* \quad (82)$$

Then the more specific Redfield equation will be

$$\frac{d}{dt} \rho_{ij}^{exc}(t) = -i\omega_{ij} \rho_{ij}^{exc}(t) + \sum_{kl} R_{ijkl} \rho_{kl}^{exc}(t) \quad (83)$$

$$R_{ijkl} = \Gamma_{ljik} + \Gamma_{kijl}^* - \delta_{jl} \sum_m \Gamma_{immk} - \delta_{ik} \sum_m \Gamma_{jmml}^* \quad (84)$$

$$\Gamma_{abcd} = \frac{1}{\hbar^2} C[\omega_{dc}] \sum_n U_{na} U_{nb}^* U_{nc} U_{nd}^* \quad (85)$$

where

$$C[\omega] = \int_0^\infty dt e^{i\omega t} C(t)$$

$$C(t) = \frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) \left[ \coth\left(\frac{\beta\hbar\omega}{2}\right) \cos\omega t - i \sin\omega t \right]$$

the real and imaginary parts of  $C[\omega]$  are expressed as

$$\text{Re}C[\omega] = \hbar J(\omega) [n_{BE}(\omega) + 1]$$

$$\text{Im}C[\omega] = \frac{1}{\pi} P \int_\infty^{-\infty} d\omega' \frac{\text{Re}C[\omega']}{\omega - \omega'}$$

respectively. From the Eq.83, we can know that

- Coherences (superpositions between states)  $\rho_{ij}(t)$  oscillating at  $\omega_{ij}$  and dephasing with a rate  $R_{ijij}$ .
- Excitonic populations  $\rho_{ii}$  which do not oscillate but are subject to population transfer with rates  $R_{iijj}(i \leftarrow j)$ .
- The other terms include transfer between coherences and populations,  $R_{iikl}$ , and can often be neglected if the chosen basis indeed is the preferred one (so-called secular approximation).

Sepecially, for the exciton population transfer reate  $R_{iijj}(i \neq j, i \leftarrow j)$ , we have

$$R_{iijj} = \Gamma_{jii} + \Gamma_{jii}^* = 2\text{Re}\Gamma_{jii} \quad (86)$$

If the system Hamiltonian is fixed

$$\Gamma_{jii} = \frac{1}{\hbar^2} C[\omega_{ji}] \sum_n^N \underline{U_{nj} U_{ni} U_{ni} U_{nj}^*} \quad (87)$$

then the underline term is also fixed. So

$$R_{iij} \propto \text{Re}C[\omega_{ji}] = \hbar J(\omega_{ji}) [n_{BE}(\omega_{ji}) + 1] \quad (88)$$

which means the positive part of  $\omega$  axis of  $\text{Re}C[\omega_{ji}]$  is in proportion to the downhill rate, negative part is in proportion to the uphill rate. The ratio of downhill and uphill rate constants between the populations of states  $|i\rangle$  and  $|j\rangle$  is always (Ref.[2])

$$\begin{aligned} \text{Ratio} \frac{\text{downhill}}{\text{uphill}} &= \frac{R_{iij}}{R_{jji}} = \frac{\hbar J(\omega_{ji}) [n_{BE}(\omega_{ji}) + 1]}{\hbar J(-\omega_{ji}) [n_{BE}(-\omega_{ji}) + 1]} = -\frac{\frac{1}{e^{\beta\hbar\omega_{ji}-1}} + 1}{\frac{1}{e^{-\beta\hbar\omega_{ji}-1}} + 1} \\ &= -\frac{\frac{1}{e^{\beta\hbar\omega_{ji}-1}} + 1}{\frac{e^{\beta\hbar\omega_{ji}}}{1-e^{\beta\hbar\omega_{ji}}} + 1} = -\frac{\frac{1}{e^{\beta\hbar\omega_{ji}-1}} + 1}{\frac{e^{\beta\hbar\omega_{ji}+1}-e^{\beta\hbar\omega_{ji}}}{1-e^{\beta\hbar\omega_{ji}}}} = -\frac{\frac{1}{e^{\beta\hbar\omega_{ji}-1}} + 1}{1-e^{\beta\hbar\omega_{ji}}} \\ &= \left( \frac{1}{e^{\beta\hbar\omega_{ji}-1}} + 1 \right) \cdot (e^{\beta\hbar\omega_{ji}} - 1) \\ &= e^{\beta\hbar\omega_{ji}} = e^{\frac{\hbar\omega_{ji}}{K_B T}} \end{aligned} \quad (89)$$

$$\text{Ratio} \frac{\text{uphill}}{\text{downhill}} = e^{-\beta\hbar\omega_{ji}} = e^{-\frac{\hbar\omega_{ji}}{K_B T}} \quad (90)$$

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