CHAPTER III

Generalized Rate Equations: The Liouville Space Approach

1 Introduction

the approach to be discussed focuses on the derivation of Generalized Rate Equations (Generalized Master Equations) for the populations $P_a(t)$ of the system eigenstates;
once such equations have been established one can easily extract the transition rates which are valid in any order of perturbation theory;

to this end we will use the projection operator technique;
since the projection operator $\mathcal{P}$ is a superoperator acting in the Liouville space formed by the usual operators, we will refer to the following treatment as the *Liouville space approach*;

in a first step we will separate the total system-reservoir Hamiltonian $H_{\rm S} + H_{\rm S-R} + H_{\rm R}$ into a zeroth-order and coupling term;
this separation starts from the expansion of $H_{\rm S-R}$ with respect to the system eigenstates;
here, we assume that the diagonal elements of $\Phi_{ab} = \langle a|H_{\rm S-R}|b\rangle$ are much larger than the off-diagonal ones;

therefore, a different treatment of the two types of couplings is reasonable;
in particular a perturbational description of the off-diagonal elements might be possible;
but the diagonal elements should be so large that they cannot be handled in a perturbation theory;

we write the system-reservoir Hamiltonian as follows

$$H = H_0 + \hat{V}$$

where the "zeroth-order" part is given by

$$H_0 = H_{\rm S} + \sum_a \Phi_{aa}(Z)|a\rangle\langle a| + H_{\rm R} \equiv \sum_a \Big(E_a + H_{\rm R} + \Phi_{aa}(Z)\Big)|a\rangle\langle a|$$

the second part suggests that we can introduce the vibrational Hamiltonian

$$H_a = E_a + H_{\rm R} + \Phi_{aa}(Z)$$

which describes the reservoir coordinate motion when the system is in its eigenstate $|a\rangle$; the perturbation $\hat{V}$ accounts for the off-diagonal elements of $\Phi_{ab}(Z)$ and reads

$$\hat{V} = \sum_{a,b}(1-\delta_{ab})\Phi_{ab}(Z)|a\rangle\langle b|$$

once the diagonal matrix elements Φ_{aa} can be accounted for exactly, a non-perturbative description of the system-reservoir coupling has been achieved;

2 Projection Operator Technique

in order to establish a nonperturbative description of the system-reservoir coupling let us introduce an appropriate projection operator;
since a simultaneous description of various states $|a\rangle$ is necessary, we generalize the projection operator $\mathcal{P}$ introduced earlier;
if the latter acts on an arbitrary operator $\hat{O}$ it reads

$$\mathcal{P}\hat{O} = \hat{R}_{\rm eq}{\rm tr}_{\rm R}\{\hat{O}\} \equiv \hat{R}_{\rm eq}\sum_{a,b}{\rm tr}_{\rm R}\{\langle a|\hat{O}|b\rangle\}|a\rangle\langle b|$$

this projector is constructed in such a way as to introduce a common equilibrium state of the reservoir modes represented by $\hat{R}_{\rm eq}$;
in contrast, the new projection operator takes the form

$$\tilde{\mathcal{P}}\hat{O} = \sum_{a}\hat{R}_{a}\,{\rm tr}_{\rm R}\{\langle a|\hat{O}|a\rangle\}|a\rangle\langle a|$$

instead of including the full state space related to the system Hamiltonian as it would be the case for the projection operator $\mathcal{P}$ the new quantity $\tilde{\mathcal{P}}$ projects on the diagonal system states matrix element; and, every system state is characterized by a separate equilibrium statistical operator

$$\hat{R}_{a} = \frac{\exp(-H_{a}/k_{\rm B}T)}{{\rm tr}_{\rm R}\{\exp(-H_{a}/k_{\rm B}T)\}}$$

the introduction of the vibrational Hamiltonians H_a consequently results in such equilibrium statistical operators;
for further use we introduce the projector $\hat{\Pi}_a = |a\rangle\langle a|$ and the combined system-reservoir equilibrium statistical operator

$$\hat{W}_a = \hat{R}_a \hat{\Pi}_a$$

if $\tilde{\mathcal{P}}$ acts on the complete statistical operator we obtain

$$\tilde{\mathcal{P}}\hat{W}(t) = \sum_a P_a(t)\hat{W}_a$$

the expression indicates a specification to the various reservoir equilibrium states (with statistical operators $\hat{R}_a$) controled by the actual population of the respective system states;
the state populations are extracted if we take the diagonal system state matrix element and the trace with respect to the reservoir state space

$$P_a(t) = \mathrm{tr}_{\mathrm{R}}\{\langle a|\tilde{\mathcal{P}}\hat{W}(t)|a\rangle\}$$

3 Generalized Rate Equations

we start with the Liouville-von Neumann equation

$$\frac{\partial}{\partial t}\hat{W}(t) = -i\mathcal{L}\hat{W}(t)$$

where

$$\mathcal{L}... = [H, ...]_-/\hbar$$

introducing the orthogonal complement

$$\tilde{\mathcal{Q}} = 1 - \tilde{\mathcal{P}}$$

a separation into two orthogonal parts yields

$$\frac{\partial}{\partial t}\tilde{\mathcal{P}}\hat{W}(t) = -i\tilde{\mathcal{P}}\mathcal{L}\left(\tilde{\mathcal{P}}\hat{W}(t) + \tilde{\mathcal{Q}}\hat{W}(t)\right)$$

and

$$\frac{\partial}{\partial t}\tilde{\mathcal{Q}}\hat{W}(t) = -i\tilde{\mathcal{Q}}\mathcal{L}\left(\tilde{\mathcal{P}}\hat{W}(t) + \tilde{\mathcal{Q}}\hat{W}(t)\right)$$

the solution of the equation for $\tilde{\mathcal{Q}}\hat{W}$ including the assumption $\tilde{\mathcal{Q}}\hat{W}(t_0) = 0$ can be written as follows

$$\tilde{\mathcal{Q}}\hat{W}(t) = -i\int_{t_0}^{t} d\bar{t}\, \mathcal{U}_{\tilde{\mathcal{Q}}}(t-\bar{t})\tilde{\mathcal{Q}}\mathcal{L}\tilde{\mathcal{P}}\hat{W}(\bar{t})$$

where the time-propagation superoperator

$$\mathcal{U}_{\tilde{\mathcal{Q}}}(t) = \exp\left\{-i\tilde{\mathcal{Q}}\mathcal{L}t\right\}$$

has been introduced; the resulting equation for $\tilde{\mathcal{P}}\hat{W}$ (the Nakjima-Zwanzig equation) is a closed equation with respect to $\tilde{\mathcal{P}}\hat{W}$ and reads

$$\frac{\partial}{\partial t}\tilde{\mathcal{P}}\hat{W}(t) = -i\tilde{\mathcal{P}}\mathcal{L}\tilde{\mathcal{P}}\hat{W}(t) - \int_{t_0}^{t} d\bar{t}\; \tilde{\mathcal{P}}\mathcal{L}\,\mathcal{U}_{\tilde{\mathcal{Q}}}(t-\bar{t})\tilde{\mathcal{Q}}\mathcal{L}\;\tilde{\mathcal{P}}\hat{W}(\bar{t})$$

in order to derive the related equations of motion for the state populations we consider the general expressions

$$\mathrm{tr}_{\mathrm{R}}\left\{\langle a|\tilde{\mathcal{P}}\mathcal{L}\hat{O}|a\rangle\right\} \equiv \mathrm{tr}_{\mathrm{R}}\left\{\langle a|\mathcal{L}\hat{O}|a\rangle\right\}$$

$\hat{O}$ may take the form

$$\hat{O}_1 = \tilde{\mathcal{P}}\hat{W}(t)$$

as well as

$$\hat{O}_2 = \mathcal{U}_{\tilde{\mathcal{Q}}}(t-\bar{t})\tilde{\mathcal{Q}}\mathcal{L}\tilde{\mathcal{P}}\hat{W}(\bar{t})$$

if we insert $\hat{O}_1$ we easily verify that the resulting expression vanishes;
the term with $\hat{O}_2$ suggests the definition of the so-called memory kernels K_{ab} of the related *Generalized Master Equation* (GME);

we, first, get

$$\mathrm{tr_R}\left\{\langle a|\mathcal{L}\hat{O}_2|a\rangle\right\} = \sum_b \mathrm{tr_R}\{\langle a|\left(\mathcal{L}\mathcal{U}_{\tilde{\mathcal{Q}}}(t-\bar{t})\tilde{\mathcal{Q}}\mathcal{L}\hat{W}_b\right)|a\rangle\}P_b(\bar{t})$$

to arrive at the memory kernel we multiply the trace expression by -1 and by the unit-step function $\theta(t-\bar{t})$ and get

$$K_{ab}(t-\bar{t}) = -\theta(t-\bar{t})\ \mathrm{tr_R}\{\langle a|\left(\mathcal{L}\mathcal{U}_{\tilde{\mathcal{Q}}}(t-\bar{t})\tilde{\mathcal{Q}}\mathcal{L}\hat{W}_b\right)|a\rangle\}$$

to set up the GME we change to $\tau = t - \bar{t}$ and obtain the following compact relation

$$\frac{\partial}{\partial t}P_a(t) = \sum_b \int_{-\infty}^{t-t_0} d\tau\ K_{ab}(\tau)P_b(t-\tau)$$

a closer inspection of the memory kernels leads to some simplifications;
first, we note that the introduction of the projector $\hat{\Pi}_a$ allows to replace the trace with respect to the reservoir states by a complete trace;
moreover, we introduce the Green's superoperator

$$\mathcal{G}_{\tilde{\mathcal{Q}}}(\tau) = -i\theta(\tau)\mathcal{U}_{\tilde{\mathcal{Q}}}(\tau)$$

and may write

$$K_{ab}(\tau) = -i\mathrm{tr}\{\hat{\Pi}_a\mathcal{L}\mathcal{G}_{\tilde{\mathcal{Q}}}(\tau)\tilde{\mathcal{Q}}\mathcal{L}\hat{W}_b\}$$

for a further simplification we separate $\mathcal{L}$ into the zeroth-order part $\mathcal{L}_0 ... = [H_0, ...]_-/\hbar$ as well as into the coupling $\mathcal{L}_V ... = [\hat{V}, ...]_-/\hbar$ and arrive at

$$\tilde{\mathcal{P}}\mathcal{L}_0 = \mathcal{L}_0\tilde{\mathcal{P}} = 0$$

these relations are is easily verified when being applied to an arbitrary operator $\hat{O}$;
in the same way we may deduce

$$\tilde{\mathcal{P}}\mathcal{L}_V\tilde{\mathcal{P}} = 0$$

using these identities and replacing $\hat{\Pi}_a\mathcal{L}$ again by $\hat{\Pi}_a\tilde{\mathcal{P}}\mathcal{L}$ we have

$$\tilde{\mathcal{P}}\mathcal{L}\mathcal{G}_{\tilde{\mathcal{Q}}}(t) = \tilde{\mathcal{P}}\mathcal{L}_V\mathcal{G}_{\tilde{\mathcal{Q}}}(t)$$

moreover, we note that

$$\tilde{\mathcal{Q}}\mathcal{L}\hat{W}_b = \tilde{\mathcal{Q}}\mathcal{L}\tilde{\mathcal{P}}\hat{W}_b = \mathcal{L}_V\hat{W}_b$$

resulting in the following notation of the memory kernels

$$K_{ab}(\tau) = -i\mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}_{\tilde{\mathcal{Q}}}(\tau)\mathcal{L}_V\hat{W}_b\} \equiv \mathrm{tr}\{\hat{\Pi}_a\mathcal{T}(\tau)\hat{W}_b\}$$

in the last expression we introduced the transfer superoperator

$$\mathcal{T}(\tau) = -i\mathcal{L}_V\mathcal{G}_{\tilde{\mathcal{Q}}}(\tau)\mathcal{L}_V$$

it offers a suitable interpretation of the memory kernel as describing probability transfer from state b to state a via time-evolution of the statistical operator $\hat{W}_b = \hat{R}_b \hat{\Pi}_b$;
the time-evolution starts at $\tau = 0$ and proceeds to $\tau > 0$ as specified by the transfer superoperator $\mathcal{T}(\tau)$;
the reservoir state-space trace and the diagonal state matrix element $\langle a|...|a\rangle$ gives the memory kernel;

finally, we notice the existence of a particular sum-rule for the memory kernels:

$$\sum_a K_{ab}(\tau) = \sum_a \mathrm{tr}\{\hat{\Pi}_a \mathcal{T}(\tau)\hat{W}_b\} = \mathrm{tr}\{\mathcal{T}(\tau)\hat{W}_b\} = 0$$

the result follows if we take into consideration that $\mathcal{T}(\tau)\hat{W}_b$ can be written as $\mathcal{L}_V$ acting on $-i\mathcal{G}_{\tilde{\mathcal{Q}}}(\tau)\mathcal{L}_V\hat{W}_b$; therefore, the trace of a commutator results which vanishes identical.

4 Rate Equations

before further dealing with the $K_{ab}(\tau)$ we briefly explain their relation to ordinary transition rates; suppose that the kernels change fast compared to the time-dependence of the populations; then, we can neglect memory effects and may write

$$\int d\tau \; K_{ab}(\tau) P_b(t-\tau) \approx \int d\tau \; K_{ab}(\tau) P_b(t)$$

we introduce the Fourier-transformed kernels

$$K_{ab}(\omega) = \int d\tau \; e^{i\omega\tau} K_{ab}(\tau)$$

and set

$$k_{ab} = K_{ab}(\omega = 0)$$

it follows an ordinary rate equation

$$\frac{\partial}{\partial t} P_a(t) = \sum_b k_{ab} P_b(t)$$

the rates are interpreted as the zero-frequency part of the Fourier-transformed kernels; the rate equations have to fulfill the conservation of total probability

$$\sum_a \frac{\partial}{\partial t} P_a(t) = 0 = \sum_{a,b} k_{ab} P_b(t)$$

the conservation is guaranteed because of the memory kernel sum-rule, which apparently remains valid after Fourier-transformation

$$0 = \sum_a k_{ab}$$

this relation yields also

$$k_{bb} = -\sum_{a \neq b} k_{ab}$$

we introduce transition rates for $a \neq b$

$$k_{ab} = k_{b \to a}$$

and obtain rate equations in their standard form

$$\frac{\partial}{\partial t} P_a = -\sum_b (k_{a \to b} P_a - k_{b \to a} P_b)$$

4.1 The Memory Kernels

for calculating rate expressions its of importance to replace the Green's superoperator $\mathcal{G}_{\tilde{\mathcal{Q}}}$ by an expression which doesn't contain the projector $\tilde{\mathcal{Q}}$;
in order to do this we, first, introduce the Fourier-transformed Green's superoperator

$$\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega) = \int dt\; e^{i\omega t}\, \mathcal{G}_{\tilde{\mathcal{Q}}}(t) = \big(\omega - \tilde{\mathcal{Q}}\mathcal{L} + i\varepsilon\big)^{-1}$$

the Fourier-transformed version of the kernel may be written as

$$K_{ab}(\omega) = -i\mathrm{tr}\{\hat{\Pi}_a \mathcal{L}_V \mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)\mathcal{L}_V \hat{W}_b\}$$

the Green's superoperator which should replace $\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)$ and which should be independent on the projector $\tilde{\mathcal{Q}}$ takes the form

$$\mathcal{G}(\omega) = \big(\omega - \mathcal{L} + i\varepsilon\big)^{-1}$$

we note the identity

$$1 = \mathcal{G}^{-1}_{\tilde{\mathcal{Q}}}(\omega)\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega) = \big(\mathcal{G}^{-1}(\omega) + \tilde{\mathcal{P}}\mathcal{L}_V\big)\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)$$

and obtain after multiplying with $\mathcal{G}$ from the left

$$\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega) = \mathcal{G}(\omega) - \mathcal{G}(\omega)\tilde{\mathcal{P}}\mathcal{L}_V \mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)$$

if this relation is inserted into the rate expression we arrive at

$$K_{ab}(\omega) = -i\mathrm{tr}\{\hat{\Pi}_a \mathcal{L}_V \mathcal{G}(\omega)\mathcal{L}_V \hat{W}_b\} + i\mathrm{tr}\{\hat{\Pi}_a \mathcal{L}_V \mathcal{G}(\omega)\tilde{\mathcal{P}}\mathcal{L}_V \mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)\mathcal{L}_V \hat{W}_b\}$$

noting the definition of $\tilde{\mathcal{P}}$ the second trace on the right-hand side can be rewritten as

$$\mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}(\omega)\tilde{\mathcal{P}}\mathcal{L}_V\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)\mathcal{L}_V\hat{W}_b\} = \sum_c \mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}(\omega)\hat{W}_c\}\ \mathrm{tr}\{\hat{\Pi}_c\mathcal{L}_V\mathcal{G}_{\tilde{\mathcal{Q}}}(\omega)\mathcal{L}_V\hat{W}_b\}$$

the second trace in the c-sum is identical to $iK_{ca}(\omega)$;
to rewrite the first trace in the c-sum we introduce the zeroth-order Green's superoperator

$$\mathcal{G}_0(\omega) = \big(\omega - \mathcal{L}_0 + i\varepsilon\big)^{-1}$$

this allows us to set up the relations

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{L}_V\mathcal{G}(\omega)$$

and

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}(\omega)\mathcal{L}_V\mathcal{G}_0(\omega)$$

both equations are a version of the ubiquitous *Dyson equation*; then, we can rearrange the first trace expression on the right-hand side of the foregoing equation as

$$\begin{aligned}\mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}(\omega)\hat{W}_c\} &= \mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}_0(\omega)\hat{W}_c\} + \mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}(\omega)\mathcal{L}_V\mathcal{G}_0(\omega)\hat{W}_c\} \\ &= \frac{1}{\omega + i\varepsilon}\mathrm{tr}\{\hat{\Pi}_a\mathcal{L}_V\mathcal{G}(\omega)\mathcal{L}_V\hat{W}_c\}\end{aligned}$$

the last line follows from the fact that trace expressions of first order in $\mathcal{L}_V$ vanish and that $\mathcal{G}_0(\omega)$ applied to $\hat{W}_c$ simply produces a frequency denominator;

we denote the kernel which doesn't depend on the projector $\tilde{\mathcal{Q}}$ as

$$L_{ab}(\omega) = -i\mathrm{tr}\{\hat{\Pi}_a \mathcal{L}_V \mathcal{G}(\omega) \mathcal{L}_V \hat{W}_b\}$$

and arrive at the following equation which relates the two types of kernels to each other

$$K_{ab}(\omega) = L_{ab}(\omega) - \frac{i}{\omega + i\varepsilon} \sum_c L_{ac}(\omega) K_{cb}(\omega)$$

once all L_{ab} have been determined the rates K_{ab} entering the rate equations can be computed according to this equation;

let us consider a perturbation expansion of L_{ab} in powers of the coupling $\hat{V}$; this expansion would be of even order in $\hat{V}$; we count the orders with respect to $\hat{V}$ by m, n and n' and get a recursion relation

$$\sum_{m=1}^{\infty} K_{ab}^{(2m)}(\omega) = \sum_{m=1}^{\infty} L_{ab}^{(2m)}(\omega) - \frac{i}{\omega + i\varepsilon} \sum_c \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} L_{ac}^{(2n)}(\omega) K_{cb}^{(2n')}(\omega)$$

in particular, the relation indicates that

$$K_{ab}^{(2)}(\omega) \equiv L_{ab}^{(2)}(\omega) = -i\mathrm{tr}\{\hat{\Pi}_a \mathcal{L}_V \mathcal{G}_0(\omega) \mathcal{L}_V \hat{W}_b\}$$

however, all higher-order contributions $K^{(2m)}$ are not only determined by $L^{(2m)}$ but also by products of lower-order rates;
when solving, for example, rate equations including rates up to a particular order m and computing related state populations, the combination of $L^{(2n)}$ with $K^{(2n')}$ ($n, n' < m$) avoids multiple counting of the lower-order rates;

4.2 Second-Order Rate Expressions

in the following we will specify the formal results of the foregoing discussion to the second-order rate; we expect a zero-frequency expression which is identical to the *Golden Rule* rate; noting the definition of $\mathcal{G}_0(\omega)$ we may write for the second-order rate

$$K_{ba}^{(2)}(\omega) = -\int_0^\infty dt\ e^{i\omega t}\mathrm{tr}_\mathrm{R}\{\langle b|\Big(\mathcal{L}_V\mathcal{U}_0(t)\mathcal{L}_V\hat{W}_a\Big)|b\rangle\}$$

we may also write

$$K_{ba}^{(2)}(\omega) = \int_0^\infty dt\ e^{i\omega t}\Big(C_{ba}(t) + \mathrm{c.c.}\Big)$$

where the correlation function is formed as

$$C_{ba}(t) = \frac{1}{\hbar^2}\mathrm{tr}_\mathrm{R}\{\langle b|U(t)\hat{V}\hat{W}_aU^+(t)\hat{V}|b\rangle\} = \frac{1}{\hbar^2}\mathrm{tr}_\mathrm{R}\{U_b(t)\Phi_{ba}\hat{R}_aU_a^+(t)\Phi_{ab}\}$$

$$= \frac{1}{\hbar^2}\mathrm{tr}_\mathrm{R}\{\hat{R}_aU_a^+(t)\Phi_{ab}U_b(t)\Phi_{ba}\}$$

we note that

$$C_{ba}^*(t) = \frac{1}{\hbar^2}\mathrm{tr}_\mathrm{R}\{\Phi_{ab}U_b(-t)\Phi_{ba}U_a^+(-t)\hat{R}_a\} = \frac{1}{\hbar^2}\mathrm{tr}_\mathrm{R}\{\hat{R}_aU_a^+(-t)\Phi_{ab}U_b(-t)\Phi_{ba}\} = C_{ba}(-t)$$

and obtain

$$K_{ba}^{(2)}(\omega) = \int_0^\infty dt\ e^{i\omega t}\Big(C_{ba}(t) + C_{ba}(-t)\Big)$$

it is also of interest to introduce the Fourier-transformed correlation function

$$C_{ba}(\omega) = \int dt\ e^{i\omega t} C_{ba}(t)$$

its zero-frequency expression as well as that of $K_{ba}^{(2)}$ give the transition rate

$$k_{a\to b} = C_{ba}(\omega = 0) = K_{ba}^{(2)}(\omega = 0)$$

we analyze $C_{ba}(\omega)$ in more detail by introducing the eigenstates (eigenvalues) $\chi_{a\mu}(\omega_{a\mu})$ and $\chi_{b\nu}(\omega_{b\nu})$ of the Hamiltonians H_a and H_b, respectively; we, first, get

$$C_{ba}(t) = \frac{1}{\hbar^2} \sum_{\mu,\nu} f_{a\mu} |\langle \chi_{a\mu} | \Phi_{ab} | \chi_{b\nu} \rangle|^2 e^{i(\omega_{a\mu} - \omega_{b\nu})t}$$

what immediately results in

$$C_{ba}(\omega) = \frac{2\pi}{\hbar^2} \sum_{\mu,\nu} f_{a\mu} |\langle \chi_{a\mu} | \Phi_{ab} | \chi_{b\nu} \rangle|^2 \delta(\omega + \omega_{a\mu} - \omega_{b\nu})$$

this expression indicates that it is a real and positive function of frequency; the equilibrium distribution $f_{a\mu}$ takes the form $\exp(-\hbar\omega_{a\mu}/k_{\mathrm{B}}T)/Z_a$ (Z_a is the state sum); the zero-frequency limit reproduces the Golden Rule rate formula;.

4.3 Fourth-Order Rate Expressions

the fourth-order (frequency-dependent) rate expression takes the form

$$K_{ba}^{(4)}(\omega) = L_{ba}^{(4)}(\omega) - \frac{i}{\omega + i\varepsilon} \sum_c K_{bc}^{(2)}(\omega) K_{ca}^{(2)}(\omega)$$

the fourth-order frequency-dependent rate $L_{ba}^{(4)}$ forms the total rate $K_{ba}^{(4)}$ after subtracting products of two second order rates; those describe transitions from the initial state $|a\rangle$ to all intermediate states $|c\rangle$ and, afterwards, from these intermediate states to the final state $|b\rangle$; the possible divergence of the prefactor $1/(\omega + i\varepsilon)$ in the zero-frequency limit indicates the need for a careful analysis; one expects a cancellation of the factorized part $\sum_c K_{bc}^{(2)} K_{ca}^{(2)}$ by parts of $L_{ba}^{(4)}$ to arrive at a finite overall fourth-order rate;
to get an expression for $L_{ba}^{(4)}(\omega)$ we note the general form of $L_{ba}(\omega)$; it indicates that the fourth-order in $\hat{V}$ is obtained if we compute the Green's superoperator up to the second order

$$\mathcal{G}(\omega) \approx \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{L}_V\mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{L}_V\mathcal{G}_0(\omega)\mathcal{L}_V\mathcal{G}_0(\omega)$$

it results

$$L_{ba}^{(4)}(\omega) = -i\mathrm{tr}\{\hat{\Pi}_b\mathcal{L}_V\mathcal{G}_0(\omega)\mathcal{L}_V\mathcal{G}_0(\omega)\mathcal{L}_V\mathcal{G}_0(\omega)\mathcal{L}_V\hat{W}_a\}$$

noting the definition of $\mathcal{G}_0(\omega)$ we may write

$$L_{ba}^{(4)}(\omega) = \int_0^\infty dt_3\ dt_2\ dt_1\ e^{i\omega(t_3+t_2+t_1)}$$

$$\times \mathrm{tr}_\mathrm{R}\{\langle b|\Big(\mathcal{L}_V\mathcal{U}_0(t_3)\mathcal{L}_V\mathcal{U}_0(t_2)\mathcal{L}_V\mathcal{U}_0(t_1)\mathcal{L}_V\hat{W}_a\Big)|b\rangle\}$$