3 Quantum State Diffusion Method I: Approach of Gaspar and Nagaoka

we follow the procedure of P. Gaspard and M. Nagaoka published in J. Chem. Phys. **111**, 5676 (1999);

3.1 System–Reservoir Separation

to generate a stochastic Schrödinger equation we note the system–reservoir separation of the Hamiltonian what results in the following standard Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = (H_{\rm S} + H_{\rm S-R} + H_{\rm R})|\Psi(t)\rangle$$

we introduce the complete basis in the state space of the reservoir $|\alpha\rangle$

$$H_{\rm R}|\alpha\rangle = E_\alpha|\alpha\rangle$$

if the reservoir is considered as a huge set of decoupled harmonic oscillators we have

$$E_\alpha = \sum_\xi \hbar\omega_\xi(N_\xi + 1/2)$$

due to the large number of oscillators which contribute, the degeneracy of the energy levels is huge; many reservoir states $|\alpha\rangle = \prod_\xi |N_\xi\rangle$ affect the active system in a similar way;

an expansion of the total state vector $|\Psi(t)\rangle$ with respect to the $|\alpha\rangle$ gives

$$|\Psi(t)\rangle = \sum_\alpha |\phi_\alpha(t)\rangle|\alpha\rangle$$

the state vector

$$|\phi_\alpha(t)\rangle = \langle\alpha|\Psi(t)\rangle$$

is the projection of the total state vector onto a particular reservoir state $|\alpha\rangle$; it is exclusively defined in the system state space; the normalization of $\Psi(t)$ results in

$$1 = \langle\Psi(t)|\Psi(t)\rangle = \sum_\alpha \langle\phi_\alpha(t)|\phi_\alpha(t)\rangle \equiv \sum_\alpha p_\alpha(t)$$

$p_\alpha(t) = \langle\phi_\alpha(t)|\phi_\alpha(t)\rangle$ is the probability at time t to have the particular reservoir state $|\alpha\rangle$ involved in $|\Psi(t)\rangle$;

the idea behind the derivation of a stochastic Schrödinger equation is that the different state vectors $\phi_\alpha(t)$ behave in a random way not only because of their mutual interaction under the time-evolution but also because of the large number of these states;
indeed, the bath's density of energy levels is very high so that the energy spectrum is very dense;
since each eigenenergy of the bath is associated with a state vectors $\phi_\alpha(t)$ in the decomposition we may understand that the time evolution of a typical state vector is affected by a very large set of state vectors;

An Additional Remark

we consider $\hat{O}_{\rm S}$ as an operator which exclusively acts in the active system state space; it's expectation value follows as

$$O_{\rm S}(t) = \langle \Psi(t) | \hat{O}_{\rm S} | \Psi(t) \rangle = \sum_{\alpha} \langle \phi_\alpha(t) | \hat{O}_{\rm S} | \phi_\alpha(t) \rangle = {\rm tr}_{\rm S}\{ \hat{\sigma}(t) \hat{O}_{\rm S} \}$$

the density operator like expression $\hat{\sigma}(t)$ takes the form

$$\hat{\sigma}(t) = \sum_{\alpha} |\phi_\alpha(t)\rangle\langle\phi_\alpha(t)| = \sum_{\alpha} p_\alpha(t) |\tilde{\phi}_\alpha(t)\rangle\langle\tilde{\phi}_\alpha(t)|$$

we introduced

$$p_\alpha(t) = \langle \phi_\alpha(t) | \phi_\alpha(t) \rangle$$

and the normalized state vectors

$$|\tilde{\phi}_\alpha(t)\rangle = |\phi_\alpha(t)\rangle / p_\alpha(t)$$

we expand the time–dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\langle\alpha|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\phi_\alpha(t)\rangle = \langle\alpha|(H_{\rm S}+H_{\rm S-R}+H_{\rm R})\sum_\beta|\phi_\beta(t)\rangle|\beta\rangle = (H_{\rm S}+E_\alpha)|\phi_\alpha(t)\rangle+\sum_\beta\langle\alpha|H_{\rm S-R}|\beta\rangle|\phi_\beta(t)\rangle$$

$$= (H_{\rm S}+E_\alpha)|\phi_\alpha(t)\rangle + \sum_u K_u \sum_\beta \langle\alpha|\Phi_u|\beta\rangle|\phi_\beta(t)\rangle$$

the time evolution of a typical coefficient, such as $\phi_\kappa(t)$ taken from all these coefficients, is affected by a very large set of coefficients which are coupled to it by the coupling matrix elements $\langle\kappa|\Phi_u|\beta\rangle$; to highlight this we change to a modified interaction representation according to

$$|\phi_\kappa(t)\rangle = e^{-i(H_{\rm S}+E_\kappa)t/\hbar}|\tilde{\phi}_\kappa(t)\rangle$$

and obtain

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\kappa(t)\rangle = \sum_u K_u^{(\rm I)}(t)\sum_\beta\langle\kappa|\Phi_u^{(\rm I)}(t)|\beta\rangle|\tilde{\phi}_\beta(t)\rangle$$

note

$$K_u^{(\rm I)}(t) = e^{iH_{\rm S}t/\hbar}K_u(t)e^{-iH_{\rm S}t/\hbar}$$

and

$$\langle\kappa|\Phi_u^{(\rm I)}(t)|\beta\rangle = e^{i\omega_{\kappa\beta}t}\langle\kappa|\Phi_u|\beta\rangle$$

we assume $\langle\kappa|\Phi_u|\kappa\rangle = 0$; then, $\tilde{\phi}_\kappa(t)$ does not appear on the right–hand side of the equation of motion for this function;

the aim of the subsequent manipulations is the derivation of a closed (and approximate) equation for $\tilde{\phi}_\kappa(t)$ (an equation where $\tilde{\phi}_\kappa(t)$ also appears on the right–hand side); therefore we start with the derivation of an equation for $\tilde{\phi}_\beta(t)$

$$|\tilde{\phi}_\beta(t)\rangle = |\tilde{\phi}_\beta(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau \sum_v K_v^{(\mathrm{I})}(\tau) \sum_{\beta'} \langle\beta|\Phi_v^{(\mathrm{I})}(\tau)|\beta'\rangle|\tilde{\phi}_{\beta'}(\tau)\rangle$$

we approximate the right–hand side by taking from the whole β'–sum only the single term with $\beta' = \kappa$

$$|\tilde{\phi}_\beta(t)\rangle \approx |\tilde{\phi}_\beta(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau \sum_v K_v^{(\mathrm{I})}(\tau)\langle\beta|\Phi_v^{(\mathrm{I})}(\tau)|\kappa\rangle|\tilde{\phi}_\kappa(\tau)\rangle$$

the equation of motion for $|\tilde{\phi}_\kappa(t)\rangle$ takes the form

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\kappa(t)\rangle = \sum_u K_u^{(\mathrm{I})}(t) \sum_\beta \langle\kappa|\Phi_u^{(\mathrm{I})}(t)|\beta\rangle|\tilde{\phi}_\beta(0)\rangle$$

$$-\frac{i}{\hbar}\sum_u K_u^{(\mathrm{I})}(t)\sum_\beta \langle\kappa|\Phi_u^{(\mathrm{I})}(t)|\beta\rangle \int_0^t d\tau \sum_v K_v^{(\mathrm{I})}(\tau)\langle\beta|\Phi_v^{(\mathrm{I})}(\tau)|\kappa\rangle|\tilde{\phi}_\kappa(\tau)\rangle$$

$$= \sum_u K_u^{(\mathrm{I})}(t)\sum_\beta \langle\kappa|\Phi_u^{(\mathrm{I})}(t)|\beta\rangle|\tilde{\phi}_\beta(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau \sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})}(\tau)\sum_\beta \langle\kappa|\Phi_u^{(\mathrm{I})}(t)|\beta\rangle\langle\beta|\Phi_v^{(\mathrm{I})}(\tau)|\kappa\rangle|\tilde{\phi}_\kappa(\tau)\rangle$$

the β–sum in the last term on the right–hand side can be removed and we finally obtain

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\kappa(t)\rangle = \sum_u K_u^{(\mathrm{I})}(t)\sum_\beta \langle\kappa|\Phi_u^{(\mathrm{I})}(t)|\beta\rangle|\tilde{\phi}_\beta(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})}(\tau)\langle\kappa|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\kappa\rangle|\tilde{\phi}_\kappa(\tau)\rangle$$

we derived an equation of motion for $|\tilde{\phi}_\kappa(t)\rangle$ where this particular state is only determined by matrix elements formed by the other states and by their initial values; an appropriate handling of these quantities will lead to the required stochastic Schrödinger equation;

3.2 Projection Operator Method

the procedure introduced in the preceding section is generalized by using the standard projection operator scheme: we introduce the projector on a representative reservoir state $|\lambda\rangle$

$$\hat{P} = 1_{\mathrm{S}}|\lambda\rangle\langle\lambda|$$

the orthogonal complement is

$$\hat{Q} = 1 - \hat{P} = 1_{\mathrm{S}} \sum_{\alpha \neq \lambda} |\alpha\rangle\langle\alpha|$$

it follows

$$\hat{P}|\Psi(t)\rangle = |\phi_\lambda(t)\rangle|\lambda\rangle$$

and

$$\hat{Q}|\Psi(t)\rangle = \sum_{\alpha \neq \lambda} |\phi_\alpha(t)\rangle|\alpha\rangle$$

we change to the interaction representation

$$|\Psi(t)\rangle = U_0(t)|\Psi^{(\mathrm{I})}(t)\rangle$$

with $U_0(t) = \exp(-i(H_{\mathrm{S}} + H_{\mathrm{R}})t/\hbar)$ and arrive at

$$|\Psi^{(\mathrm{I})}(t)\rangle = U_0^+(t) \sum_\alpha |\phi_\alpha(t)\rangle|\alpha\rangle = \sum_\alpha e^{i(H_{\mathrm{S}}+E_\alpha)t/\hbar}|\phi_\alpha(t)\rangle|\alpha\rangle = \sum_\alpha |\tilde{\phi}_\alpha(t)\rangle|\alpha\rangle$$

we use

$$|\tilde{\phi}_\alpha(t)\rangle = e^{i(H_{\mathrm{S}}+E_\lambda)t/\hbar}|\phi_\alpha(t)\rangle$$

and obtain

$$\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle = 1_{\mathrm{S}}|\lambda\rangle\langle\lambda||\Psi^{(\mathrm{I})}(t)\rangle = |\tilde{\phi}_\lambda(t)\rangle|\lambda\rangle$$

noting the time–dependent Schrödinger equation in the interaction representation

$$i\hbar\frac{\partial}{\partial t}|\Psi^{(\mathrm{I})}(t)\rangle = H^{(\mathrm{I})}_{\mathrm{S-R}}(t)|\Psi^{(\mathrm{I})}(t)\rangle$$

we may deduce

$$i\hbar\frac{\partial}{\partial t}\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle = \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle + \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\times\hat{Q}|\Psi^{(\mathrm{I})}(t)\rangle$$

and

$$i\hbar\frac{\partial}{\partial t}\hat{Q}|\Psi^{(\mathrm{I})}(t)\rangle = \hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle + \hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\times\hat{Q}|\Psi^{(\mathrm{I})}(t)\rangle$$

to achieve a formal solution of the latter equation we introduce

$$\hat{S}_Q(t) = \hat{T}\exp\Big(-\frac{i}{\hbar}\int_0^t d\tau\ \hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{Q}\Big)$$

and get

$$\hat{Q}|\Psi^{(\mathrm{I})}(t)\rangle = \hat{S}_Q(t)\hat{Q}|\Psi^{(\mathrm{I})}(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau\ \hat{S}_Q(t-\tau)\hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(\tau)\rangle$$

inserting this equation into the one for $\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle$ gives

$$i\hbar\frac{\partial}{\partial t}\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle = \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle + \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\hat{S}_Q(t)\hat{Q}|\Psi^{(\mathrm{I})}(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\times\hat{S}_Q(t-\tau)\times\hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(\tau)\rangle$$

for a further treatment all expressions of $H^{(\mathrm{I})}_{\mathrm{S-R}}$ combined with the projectors are calculated

$$\hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P} = 1_{\mathrm{S}}|\lambda\rangle\langle\lambda|\sum_u K^{(\mathrm{I})}_u(t)\Phi^{(\mathrm{I})}_u(t)1_{\mathrm{S}}|\lambda\rangle\langle\lambda| = \sum_u K^{(\mathrm{I})}_u(t)\langle\lambda|\Phi^{(\mathrm{I})}_u(t)|\lambda\rangle|\lambda\rangle\langle\lambda|$$

and

$$\hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q} = 1_{\mathrm{S}}|\lambda\rangle\langle\lambda|\sum_u K^{(\mathrm{I})}_u(t)\Phi^{(\mathrm{I})}_u(t)1_{\mathrm{S}}\sum_{\alpha\neq\lambda}|\alpha\rangle\langle\alpha|$$

$$= \sum_u K^{(\mathrm{I})}_u(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi^{(\mathrm{I})}_u(t)|\alpha\rangle|\lambda\rangle\langle\alpha|$$

and

$$\hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P} = \sum_u K^{(\mathrm{I})+}_u(t)\sum_{\alpha\neq\lambda}\langle\alpha|\Phi^{(\mathrm{I})+}_u(t)|\lambda\rangle|\alpha\rangle\langle\lambda|$$

and finally

$$\hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q} = \sum_u K^{(\mathrm{I})}_u(t)\sum_{\alpha\neq\lambda}\sum_{\beta\neq\lambda}\langle\alpha|\Phi^{(\mathrm{I})}_u(t)|\beta\rangle|\alpha\rangle\langle\beta|$$

3.3 Second Order Expansion

for further considerations we concentrate on a second order with respect to the system reservoir coupling; therefore we approximate

$$\hat{S}_Q(t) \approx 1 - \frac{i}{\hbar}\int_0^t d\tau\ \hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{Q}$$

it gives

$$i\hbar\frac{\partial}{\partial t}\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle \approx \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle + \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\Big(1 - \frac{i}{\hbar}\int_0^t d\tau\ \hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{Q}\Big)\hat{Q}|\Psi^{(\mathrm{I})}(0)\rangle$$
$$-\frac{i}{\hbar}\int_0^t d\tau\ \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\times\hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(\tau)\rangle$$

we further note

$$\frac{\partial}{\partial t}\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle = |\lambda\rangle\frac{\partial}{\partial t}|\tilde{\phi}_\lambda(t)\rangle$$

and

$$\hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(t)\rangle = \sum_u K^{(\mathrm{I})}_u(t)\langle\lambda|\Phi^{(\mathrm{I})}_u(t)|\lambda\rangle|\lambda\rangle\langle\lambda||\tilde{\phi}_\lambda(t)\rangle|\lambda\rangle$$
$$= \sum_u K^{(\mathrm{I})}_u(t)\langle\lambda|\Phi^{(\mathrm{I})}_u(t)|\lambda\rangle|\tilde{\phi}_\lambda(t)\rangle|\lambda\rangle$$

this term vanishes since we assume $\langle\lambda|\Phi^{(\mathrm{I})}_u(t)|\lambda\rangle = 0$;

next we compute

$$\hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\Big(1-\frac{i}{\hbar}\int_0^t d\tau\ \hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{Q}\Big)\hat{Q}|\Psi^{(\mathrm{I})}(0)\rangle =$$

$$\sum_u K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle|\lambda\rangle\langle\alpha|\Big(1-\frac{i}{\hbar}\int_0^t d\tau\ \sum_v K_v^{(\mathrm{I})}(\tau)\sum_{\alpha'\neq\lambda}\sum_{\beta'\neq\lambda}\langle\alpha'|\Phi_v^{(\mathrm{I})}(\tau)|\beta'\rangle|\alpha'\rangle\langle\beta'|\Big)\sum_{\beta\neq\lambda}|\tilde{\phi}_\beta(0)\rangle|\beta\rangle$$

$$= \sum_u K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle|\lambda\rangle|\tilde{\phi}_\alpha(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v}K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\sum_{\beta\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle|\lambda\rangle K_v^{(\mathrm{I})}(\tau)\langle\alpha|\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle|\tilde{\phi}_\beta(0)\rangle$$

$$= |\lambda\rangle\sum_u K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle|\tilde{\phi}_\alpha(0)\rangle$$

$$-|\lambda\rangle\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v}K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})}(\tau)\sum_{\alpha\neq\lambda}\sum_{\beta\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle\langle\alpha|\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle|\tilde{\phi}_\beta(0)\rangle$$

we again assume $\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\lambda\rangle = 0$ and obtain

$$\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle\langle\alpha|\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle = \langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle$$

finally we calculate

$$-\frac{i}{\hbar}\int_0^t d\tau\ \hat{P}H^{(\mathrm{I})}_{\mathrm{S-R}}(t)\hat{Q}\times\hat{Q}H^{(\mathrm{I})}_{\mathrm{S-R}}(\tau)\hat{P}\times\hat{P}|\Psi^{(\mathrm{I})}(\tau)\rangle =$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \sum_u K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle|\lambda\rangle\langle\alpha|\sum_v K_v^{(\mathrm{I})+}(\tau)\sum_{\beta\neq\lambda}\langle\beta|\Phi_v^{(\mathrm{I})+}(\tau)|\lambda\rangle|\beta\rangle\langle\lambda||\tilde{\phi}_\lambda(\tau)\rangle|\lambda\rangle$$

$$= -|\lambda\rangle\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v}K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})+}(\tau)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle\langle\alpha|\Phi_v^{(\mathrm{I})+}(\tau)|\lambda\rangle|\tilde{\phi}_\lambda(\tau)\rangle$$

multiplying the equation of motion with $\langle\lambda|$ gives (note the assumption $\Phi_u^+ = \Phi_u$)

$$\frac{\partial}{\partial t}|\tilde{\phi}_\lambda(t)\rangle = \sum_u K_u^{(\mathrm{I})}(t)\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\lambda\rangle|\tilde{\phi}_\lambda(t)\rangle + \sum_u K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle|\tilde{\phi}_\alpha(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})}(\tau)\sum_{\beta\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle|\tilde{\phi}_\beta(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})+}(\tau)\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\lambda\rangle|\tilde{\phi}_\lambda(\tau)\rangle$$

we note $\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\lambda\rangle = 0$ in the first term on the right–hand side and get

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\lambda(t)\rangle = \sum_u K_u^{(\mathrm{I})}(t)\sum_{\alpha\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle \times |\tilde{\phi}_\alpha(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})}(\tau)\sum_{\beta\neq\lambda}\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle \times |\tilde{\phi}_\beta(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau\ \sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})+}(\tau)\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\lambda\rangle \times |\tilde{\phi}_\lambda(\tau)\rangle$$

we introduce the forcing term

$$\hat{F}_\lambda(t) = \sum_u K_u^{(\mathrm{I})}(t) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle \times |\tilde{\phi}_\alpha(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau \sum_{u,v} K_u^{(\mathrm{I})}(t) K_v^{(\mathrm{I})}(\tau) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\alpha\rangle \times |\tilde{\phi}_\alpha(0)\rangle$$

it is determined by the initial state; it acts as a stochastic force due to the reservoir fluctuations; the remaining term with $|\tilde{\phi}_\lambda(\tau)\rangle$ at earlier time τ represents the damping term; it follows

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\lambda(t)\rangle = \hat{F}_\lambda(t) - \frac{i}{\hbar}\int_0^t d\tau \sum_{u,v} K_u^{(\mathrm{I})}(t) K_v^{(\mathrm{I})+}(\tau) \langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})+}(\tau)|\lambda\rangle|\tilde{\phi}_\lambda(\tau)\rangle$$

the forcing term can be rewritten as

$$\hat{F}_\lambda(t) = \sum_u K_u^{(\mathrm{I})}(t) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle \times |\tilde{\phi}_\alpha(0)\rangle$$

$$+\sum_u K_u^{(\mathrm{I})}(t) \sum_\beta \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\beta\rangle \frac{(-i)}{\hbar}\int_0^t d\tau \sum_v K_v^{(\mathrm{I})}(\tau) \sum_{\alpha\neq\lambda} \langle\beta|\Phi_v^{(\mathrm{I})}(\tau)|\alpha\rangle \times |\tilde{\phi}_\alpha(0)\rangle$$

$$= \sum_u K_u^{(\mathrm{I})}(t) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle$$

$$\left\{|\tilde{\phi}_\alpha(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau \sum_v K_v^{(\mathrm{I})}(\tau) \sum_{\beta\neq\lambda} \langle\alpha|\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle \times |\tilde{\phi}_\beta(0)\rangle\right\}$$

in the last term an interchange of α and β has been taken; comparing the expression in the wavy bracket with the integrated time–dependent Schrödinger equation

$$|\tilde{\phi}_\alpha(t)\rangle = |\tilde{\phi}_\alpha(0)\rangle - \frac{i}{\hbar}\int_0^t d\tau \sum_v K_v^{(\mathrm{I})}(\tau) \sum_\beta \langle\alpha|\Phi_v^{(\mathrm{I})}(\tau)|\beta\rangle|\tilde{\phi}_\beta(\tau)\rangle$$

we realize the following notation

$$\hat{F}_\lambda(t) = \sum_u K_u^{(\mathrm{I})}(t) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle \times |\tilde{\phi}_\alpha^{(1)}(t)\rangle$$

where $|\tilde{\phi}_\alpha^{(1)}(t)\rangle$ is the time–dependent state vector determined in the first order of the system–reservoir coupling; we will make use of this result later;

3.4 Statistical Typicality

in order to obtain a stochastic differential equation, we need to assume that the $|\tilde{\phi}_\lambda(t)\rangle$ represent statistically each one of the $|\tilde{\phi}_\alpha(t)\rangle$ of the linear decomposition

$$|\Psi^{(\mathrm{I})}(t)\rangle = \sum_\alpha |\tilde{\phi}_\alpha(t)\rangle|\alpha\rangle$$

of the total wave function in the interaction picture;
in this sense, we should assume that all the $|\tilde{\phi}_\alpha(t)\rangle$ behave similarly and form a statistical ensemble for which $|\tilde{\phi}_\lambda(t)\rangle$ is a typical representative; this assumption shall be called the assumption of *statistical typicality*;

the assumption of statistical typicality can be justified if the bath subsystem is classically chaotic; namely, the average of a bath operator $\mathcal{B}$ over a typical eigenstate $|\lambda\rangle$ is essentially equivalent to a classical average over the microcanonical statistical ensemble at the energy equal to the eigenenergy E_λ; this behavior has its origin in the property that typical eigenfunctions are statistically irregular at high quantum numbers; moreover, since the bath is a large subsystem, this microcanonical average is essentially equivalent to a canonical average

$$\langle\lambda|\mathcal{B}|\lambda\rangle \approx \mathrm{tr}_\mathrm{R}\{\hat{R}_\mathrm{eq}\mathcal{B}\}$$

where

$$\hat{R}_\mathrm{eq} = \frac{1}{\mathcal{Z}} e^{-H_\mathrm{R}/k_\mathrm{B}T}$$

as a consequence of the assumption of statistical typicality of the $|\tilde{\phi}_\lambda(t)\rangle$ we obtain for the correlation function in the damping term of the time–dependent Schrödinger equation (note the assumption $\Phi_v^{(\mathrm{I})+} = \Phi_v^{(\mathrm{I})}$)

$$\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})+}(\tau)|\lambda\rangle \approx \mathrm{tr}_\mathrm{R}\{\hat{R}_\mathrm{eq}\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)\} \equiv \hbar^2 C_{uv}(t-\tau)$$

the form of the damping term should be essentially independent of the particular state vector that has been chosen among the ensemble of state vectors; obviously the correlation function is the one appearing in the standard quantum master equation;

in order to obtain the typical behavior of the forcing term, we need to make assumptions on the initial condition of the total wave function;
$|\Psi(t=0)\rangle$ is assumed to be a pure state; in order to construct it we assume

$$\langle\Psi(0)|\hat{O}|\Psi(0)\rangle \approx \mathrm{tr}\{|\psi(0)\rangle\langle\psi(0)|\hat{R}_\mathrm{eq}\hat{O}\}$$

$\psi(0)$ is the system wave function at the initial time (it is normalized to 1) and $\hat{O}$ is an operator acting in the complete state space of the system plus the reservoir;
we replace the reservoir part of the trace by an expansion with respect to the reservoir states $|\alpha\rangle$

$$\langle\Psi(0)|\hat{O}|\Psi(0)\rangle \approx \sum_\alpha \langle\alpha|\mathrm{tr}_\mathrm{S}\{|\psi(0)\rangle\langle\psi(0)|\hat{R}_\mathrm{eq}\hat{O}\}|\alpha\rangle = \sum_\alpha f_\alpha \mathrm{tr}_\mathrm{S}\{|\psi(0)\rangle\langle\psi(0)|\langle\alpha|\hat{O}|\alpha\rangle\}$$

note

$$f_\alpha = \frac{1}{\mathcal{Z}} e^{-E_\alpha/k_\mathrm{B}T}$$

the approximate equality for $\langle\Psi(0)|\hat{O}|\Psi(0)\rangle$ can be established under the assumption that the initial condition of the total wave function is given by

$$|\Psi(0)\rangle \approx |\psi(0)\rangle \sum_\alpha \sqrt{f_\alpha} e^{i\theta_\alpha} |\alpha\rangle$$

the θ_α are random phases distributed between 0 and 2π; we obtain

$$\langle\Psi(0)|\hat{O}|\Psi(0)\rangle \approx \sum_{\alpha,\beta} \langle\psi(0)|\sqrt{f_\alpha} e^{-i\theta_\alpha} \langle\alpha|\hat{O}\sqrt{f_\beta} e^{i\theta_\beta}|\beta\rangle|\psi(0)\rangle$$

an additional averaging with respect to the random phases would let remain the terms with $\alpha = \beta$ only; this gives the required result;
the introduced assumption for $\Psi(0)$ implies that the initial conditions of the $\phi_\alpha(t)$ related to the decomposition

$$|\Psi(t)\rangle = \sum_\alpha |\phi_\alpha(t)\rangle|\alpha\rangle$$

take the form

$$|\phi_\alpha(0)\rangle = |\tilde{\phi}_\alpha(0)\rangle = |\psi(0)\rangle \sqrt{f_\alpha} e^{i\theta_\alpha}$$

an important consequence of this relation is that all the initial functions are proportional to the same initial wave function of the system; in particular, the chosen state vector $|\tilde{\phi}_\lambda(t)\rangle$ is also proportional to the same initial wave function because the relation also holds for the special function with $\alpha = \lambda$; hence, we find that

$$|\tilde{\phi}_\alpha(0)\rangle \approx |\tilde{\phi}_\lambda(0)\rangle e^{-(E_\alpha - E_\lambda)/2k_\mathrm{B}T} e^{i(\theta_\alpha - \theta_\lambda)}$$

the forcing term becomes

$$\hat{F}_\lambda(t) \approx \sum_u K_u^{(\mathrm{I})}(t) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle e^{-(E_\alpha-E_\lambda)/2k_\mathrm{B}T} e^{i(\theta_\alpha-\theta_\lambda)}|\tilde{\phi}_\lambda(0)\rangle$$

$$-\frac{i}{\hbar}\int_0^t d\tau \sum_{u,v} K_u^{(\mathrm{I})}(t) K_v^{(\mathrm{I})}(\tau) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)|\alpha\rangle e^{-(E_\alpha-E_\lambda)/2k_\mathrm{B}T} e^{i(\theta_\alpha-\theta_\lambda)}|\tilde{\phi}_\lambda(0)\rangle$$

$$\approx \sum_u K_u^{(\mathrm{I})}(t) \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle e^{-(E_\alpha-E_\lambda)/2k_\mathrm{B}T} e^{i(\theta_\alpha-\theta_\lambda)}|\tilde{\phi}_\lambda(t)\rangle$$

in the last step we have supposed that the second term in the perturbative expansion gives an approximation for the time evolution of $|\tilde{\phi}_\lambda(t)\rangle$;
we finally write

$$\hat{F}_\lambda(t) = \sum_u \eta_u(t) K_u^{(\mathrm{I})}(t)|\tilde{\phi}_\lambda(t)\rangle$$

with the noise terms

$$\eta_u(t) = \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\mathrm{I})}(t)|\alpha\rangle e^{-(E_\alpha-E_\lambda)/2k_\mathrm{B}T} e^{i(\theta_\alpha-\theta_\lambda)}$$

the Schrödinger equation can bewritten as

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\lambda(t)\rangle = \sum_u \eta_u(t) K_u^{(\mathrm{I})}(t)|\tilde{\phi}_\lambda(t)\rangle - \frac{i}{\hbar}\int_0^t d\tau \sum_{u,v} K_u^{(\mathrm{I})}(t) K_v^{(\mathrm{I})+}(\tau)\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})+}(\tau)|\lambda\rangle|\tilde{\phi}_\lambda(\tau)\rangle$$

we may use the earlier derived relation

$$\langle\lambda|\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})+}(\tau)|\lambda\rangle \approx \mathrm{tr}_\mathrm{R}\{\hat{R}_\mathrm{eq}\Phi_u^{(\mathrm{I})}(t)\Phi_v^{(\mathrm{I})}(\tau)\} \equiv \hbar^2 C_{uv}(t-\tau)$$

the random distribution of the phases between 0 and 2π results in the following simple phase averaging formula

$$< f(\theta) >_{\rm ph} = \frac{1}{2\pi}\int_0^{2\pi} d\theta\ f(\theta)$$

it simply results

$$< e^{i\theta} >_{\rm ph} = \frac{1}{2\pi}\int_0^{2\pi} d\theta\ e^{i\theta} = 0$$

next we consider $< e^{i(\theta+\theta')} >_{\rm ph}$; here, θ and θ' may belong to different states of the reservoir; in this case we get

$$< e^{i(\theta+\theta')} >_{\rm ph} = < e^{i\theta} >_{\rm ph} \times < e^{i\theta'} >_{\rm ph} = 0$$

if they belong to the same state we arrive at

$$< e^{i2\theta} >_{\rm ph} = 0$$

if one considers, however $< e^{i(\theta-\theta')} >_{\rm ph}$ we get also zero for the case that θ and θ' belong to different states of the reservoir; we get 1 if they belong to the same reservoir state; turning to an averaging of expressions including different $\eta_u(t)$ we first consider

$$< \eta_u(t) >_{\rm ph} = \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\rm I)}(t)|\alpha\rangle e^{-(E_\alpha-E_\lambda)/2k_{\rm B}T} < e^{i(\theta_\alpha-\theta_\lambda)} >_{\rm ph} = 0$$

the result is obtained since $\alpha \neq \lambda$;

next, we consider

$$< \eta_u(t)\eta_v(\tau) >_{\rm ph} = \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\rm I)}(t)|\alpha\rangle e^{-(E_\alpha - E_\lambda)/2k_{\rm B}T} \sum_{\beta\neq\lambda} \langle\lambda|\Phi_v^{(\rm I)}(\tau)|\beta\rangle e^{-(E_\beta - E_\lambda)/2k_{\rm B}T}$$

$$< e^{i(\theta_\alpha - \theta_\lambda)} e^{i(\theta_\beta - \theta_\lambda)} >_{\rm ph} = 0$$

finally we consider

$$< \eta_u(t)\eta_v^*(\tau) >_{\rm ph} = \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\rm I)}(t)|\alpha\rangle e^{-(E_\alpha - E_\lambda)/2k_{\rm B}T} \sum_{\beta\neq\lambda} \langle\beta|\Phi_v^{(\rm I)}(\tau)|\lambda\rangle e^{-(E_\beta - E_\lambda)/2k_{\rm B}T}$$

$$< e^{i(\theta_\alpha - \theta_\lambda)} e^{-i(\theta_\beta - \theta_\lambda)} >_{\rm ph}$$

$$= e^{E_\lambda/k_{\rm B}T} \sum_{\alpha\neq\lambda} \langle\lambda|\Phi_u^{(\rm I)}(t)|\alpha\rangle e^{-E_\alpha/k_{\rm B}T} \langle\alpha|\Phi_v^{(\rm I)}(\tau)|\lambda\rangle$$

$$= \mathcal{Z} e^{E_\lambda/k_{\rm B}T} \langle\lambda|\Phi_u^{(\rm I)}(t)\hat{R}_{\rm eq}\Phi_v^{(\rm I)}(\tau)|\lambda\rangle$$

in order to obtain a typical value for these correlation functions we perform a thermal average

$$\sum_\lambda \frac{e^{-E_\lambda/k_{\rm B}T}}{\mathcal{Z}} < \eta_u(t)\eta_v^*(\tau) >_{\rm ph} = \sum_\lambda \langle\lambda|\Phi_u^{(\rm I)}(t)\hat{R}_{\rm eq}\Phi_v^{(\rm I)}(\tau)|\lambda\rangle$$

$$= {\rm tr}_{\rm R}\{\hat{R}_{\rm eq}\Phi_v^{(\rm I)}(\tau)\Phi_u^{(\rm I)}(t)\} = \hbar^2 C_{vu}(\tau,t) = \hbar^2 C_{uv}^*(t,\tau)$$

so we identify

$$< \eta_u(t)\eta_v^*(\tau) >_{\rm ph} = \hbar^2 C_{vu}(\tau,t)$$

and

$$< \eta_u^*(t)\eta_v(\tau) >_{\rm ph} = \hbar^2 C_{uv}(t,\tau)$$

3.6 The Stochastic Schrödinger Equation

the reasoning used in the preceding section also allows to introduce the correlation funtion in the damping term of the time–dependent Schrödinger equation; it follows

$$i\hbar\frac{\partial}{\partial t}|\tilde{\phi}_\lambda(t)\rangle = \sum_u \eta_u(t)K_u^{(\mathrm{I})}(t)|\tilde{\phi}_\lambda(t)\rangle - i\hbar\int_0^t d\tau \sum_{u,v} K_u^{(\mathrm{I})}(t)K_v^{(\mathrm{I})+}(\tau)C_{uv}(t-\tau)|\tilde{\phi}_\lambda(\tau)\rangle$$

a single $|\tilde{\phi}_\lambda(t)\rangle$ is representative for all $|\tilde{\phi}_\lambda(t)\rangle$; so the quantum number λ can be removed; we introduce

$$|\psi(t)\rangle = e^{-iH_\mathrm{S}t/\hbar}|\tilde{\phi}_\lambda(t)\rangle = e^{iE_\kappa t/\hbar}|\phi_\lambda(t)\rangle$$

and arrive at

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H_\mathrm{S}|\psi(t)\rangle + \sum_u \eta_u(t)K_u|\psi(t)\rangle - i\hbar\int_0^t d\tau \sum_{u,v} C_{uv}(t-\tau)K_u e^{-iH_\mathrm{S}(t-\tau)/\hbar}K_v|\psi(\tau)\rangle$$

if a statistical ensemble of initial states $\psi_j(0)$ is considered, the different $\psi_j(t)$ obey the stochastic Schrödinger equation (note the change from τ to $t-\tau$)

$$i\hbar\frac{\partial}{\partial t}|\psi_j(t)\rangle = H_\mathrm{S}|\psi_j(t)\rangle + \sum_u \eta_u(t)K_u|\psi_j(t)\rangle - i\hbar\int_0^t d\tau \sum_{u,v} C_{uv}(\tau)K_u e^{-iH_\mathrm{S}(\tau)/\hbar}K_v|\psi_j(t-\tau)\rangle$$

the related density operator follows as

$$\hat{\rho}(t) = \sum_j w_j \frac{< |\psi_j(t)\rangle\langle\psi_j(t| >_\mathrm{ph}}{< \langle\psi_j(t|\psi_j(t)\rangle >_\mathrm{ph}}$$

the stochastic terms are defined via colored Gaussian noise (a single u is considered here only)

$$< \eta(t) >= 0 \qquad < \eta(t)\eta(0) >= 0 \qquad < \eta^*(t)\eta(0) >= C(t)$$

such a noise can be generated according to

$$\eta(t) = \int d\tau \ R(\tau) \frac{\xi_1(t-\tau) + i\xi_2(t-\tau)}{\sqrt{2}}$$

ξ_1 and ξ_2 are two indipendent Gaussian white noise processes

$$< \xi_{1,2}(t) >= 0 \qquad < \xi_1(t)\xi_2(0) >= 0 \qquad < \xi_1(t)\xi_1(0) >=< \xi_2(t)\xi_2(0) >= \delta(t)$$

the function $R(\tau)$ which translates Gaussian white noise into colored Gaussian noise is defined by

$$C(t) = \int_0^\infty d\tau \ R^*(t+\tau)R(\tau)$$

we change back to $|\tilde{\phi}(t)\rangle$ and write

$$i\hbar \frac{\partial}{\partial t}|\tilde{\phi}(t)\rangle = \Delta H^{(\mathrm{I})}(t)|\tilde{\phi}(t)\rangle - i\hbar \int_0^t d\tau\ M^{(\mathrm{I})}(t,\tau)|\tilde{\phi}(\tau)\rangle$$

where we introduced

$$\Delta H^{(\mathrm{I})}(t) = \sum_u \eta_u(t) K_u^{(\mathrm{I})}(t)$$

and

$$M^{(\mathrm{I})}(t,\tau) = \sum_{u,v} K_u^{(\mathrm{I})}(t) K_v^{(\mathrm{I})}(\tau) C_{uv}(t-\tau)$$

we construct a noise averaged density operator

$$\hat{\sigma}(t) =< |\tilde{\phi}(t)\rangle\langle\tilde{\phi}(t)| >_{\mathrm{ph}}$$

and derive an equation of motion; the solution of the Schrödinger equation up to the second order in the system–reservoir coupling reads

$$|\tilde{\phi}(t)\rangle = |\tilde{\phi}(0)\rangle - \frac{i}{\hbar}\int_0^t dt_1\ \Delta H^{(\mathrm{I})}(t_1)|\tilde{\phi}(0)\rangle - \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2\ \Delta H^{(\mathrm{I})}(t_1)\Delta H^{(\mathrm{I})}(t_2)|\tilde{\phi}(0)\rangle$$
$$- \int_0^t dt_1 \int_0^{t_1} dt_2\ M^{(\mathrm{I})}(t_1,t_2)|\tilde{\phi}(0)\rangle$$

the noise averaged density operator follows as

$$\hat{\sigma}(t) = \hat{\sigma}(0) + \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^t dt_2 \ < \Delta H^{(\mathrm{I})}(t_1)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_2) >_{\mathrm{ph}}$$

$$-\frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2 \ < \Delta H^{(\mathrm{I})}(t_1)\Delta H^{(\mathrm{I})}(t_2) >_{\mathrm{ph}} \hat{\sigma}(0) - \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2 \ \hat{\sigma}(0) < \Delta H^{(\mathrm{I})+}(t_2)\Delta H^{(\mathrm{I})+}(t_1) >_{\mathrm{ph}}$$

$$-\int_0^t dt_1 \int_0^{t_1} dt_2 \ M^{(\mathrm{I})}(t_1,t_2)\hat{\sigma}(0) - \int_0^t dt_1 \int_0^{t_1} dt_2 \ \hat{\sigma}(0) M^{(\mathrm{I})+}(t_1,t_2)$$

we note

$$< \Delta H^{(\mathrm{I})}(t_1)\Delta H^{(\mathrm{I})}(t_2) >_{\mathrm{ph}} = < \Delta H^{(\mathrm{I})+}(t_2)\Delta H^{(\mathrm{I})+}(t_1) >_{\mathrm{ph}} = 0$$

and

$$I(t) = \int_0^t dt_1 \int_0^t dt_2 \ < \Delta H^{(\mathrm{I})}(t_1)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_2) >_{\mathrm{ph}}$$

$$= \int_0^t dt_1 \int_0^{t_1} dt_2 \ \big(< \Delta H^{(\mathrm{I})}(t_1)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_2) >_{\mathrm{ph}} + < \Delta H^{(\mathrm{I})}(t_2)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_1) >_{\mathrm{ph}} \big)$$

note that the norm of $|\tilde{\phi}(t)\rangle$ does not change up to the second order in the system–reservoir coupling;

so the density operator takes the form

$$\hat{\sigma}(t) = \hat{\sigma}(0)$$

$$+\frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2 \ < \Delta H^{(\mathrm{I})}(t_1)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_2) >_{\mathrm{ph}} + \frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2 \ < \Delta H^{(\mathrm{I})}(t_2)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_1) >_{\mathrm{ph}}$$

$$-\int_0^t dt_1 \int_0^{t_1} dt_2 \left(M^{(\mathrm{I})}(t_1,t_2)\hat{\sigma}(0) + \hat{\sigma}(0)M^{(\mathrm{I})+}(t_1,t_2)\right)$$

we remember $< \eta_u(t)\eta_v^*(\tau) >_{\mathrm{ph}} \sim C_{vu}(\tau, t)$ and get

$$< \Delta H^{(\mathrm{I})}(t_1)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_2) >_{\mathrm{ph}} = \hbar^2 \sum_{u,v} C_{vu}(t_2 - t_1)K_u^{(\mathrm{I})}(t_1)\hat{\sigma}(0)K_v^{(\mathrm{I})}(t_2)$$

$$< \Delta H^{(\mathrm{I})}(t_2)\hat{\sigma}(0)\Delta H^{(\mathrm{I})+}(t_1) >_{\mathrm{ph}} = \hbar^2 \sum_{u,v} C_{uv}(t_1 - t_2)K_v^{(\mathrm{I})}(t_2)\hat{\sigma}(0)K_u^{(\mathrm{I})}(t_1)$$

$$M^{(\mathrm{I})}(t_1,t_2) = \sum_{u,v} K_u^{(\mathrm{I})}(t_1)K_v^{(\mathrm{I})}(t_2)C_{uv}(t_1 - t_2)$$

and

$$M^{(\mathrm{I})+}(t_1,t_2) = \sum_{u,v} K_v^{(\mathrm{I})}(t_2)K_u^{(\mathrm{I})}(t_1)C^*_{uv}(t_1 - t_2)$$

before using these relations we change to $\tau = t_1$ and $\tau' = t_1 - t_2$, i.e. $t_2 = \tau - \tau'$

$$\hat{\sigma}(t) = \hat{\sigma}(0)$$

$$+ \int_0^t d\tau \int_0^\tau d\tau' \left\{ \frac{1}{\hbar^2} < \Delta H^{(\mathrm{I})}(\tau) \hat{\sigma}(0) \Delta H^{(\mathrm{I})+}(\tau - \tau') >_{\mathrm{ph}} + \frac{1}{\hbar^2} < \Delta H^{(\mathrm{I})}(\tau - \tau') \hat{\sigma}(0) \Delta H^{(\mathrm{I})+}(\tau) >_{\mathrm{ph}} \right.$$

$$\left. - M^{(\mathrm{I})}(\tau, \tau - \tau') \hat{\sigma}(0) - \hat{\sigma}(0) M^{(\mathrm{I})+}(\tau, \tau - \tau') \right\}$$

and arrive at

$$\hat{\sigma}(t) = \hat{\sigma}(0) + \int_0^t d\tau \int_0^\tau d\tau' \sum_{u,v} \left\{ C^*_{uv}(\tau') K_u^{(\mathrm{I})}(\tau) \hat{\sigma}(0) K_v^{(\mathrm{I})}(\tau - \tau') + C_{uv}(\tau') K_v^{(\mathrm{I})}(\tau - \tau') \hat{\sigma}(0) K_u^{(\mathrm{I})}(\tau) \right.$$

$$\left. - C_{uv}(\tau') K_u^{(\mathrm{I})}(\tau) K_v^{(\mathrm{I})}(\tau - \tau') \hat{\sigma}(0) - C^*_{uv}(\tau') \hat{\sigma}(0) K_v^{(\mathrm{I})}(\tau - \tau') K_u^{(\mathrm{I})}(\tau) \right\}$$

the time–derivative gives

$$\frac{\partial}{\partial t} \hat{\sigma}(t) = \int_0^t d\tau' \sum_{u,v} \left\{ C^*_{uv}(\tau') K_u^{(\mathrm{I})}(t) \hat{\sigma}(0) K_v^{(\mathrm{I})}(t - \tau') + C_{uv}(\tau') K_v^{(\mathrm{I})}(t - \tau') \hat{\sigma}(0) K_u^{(\mathrm{I})}(t) \right.$$

$$\left. - C_{uv}(\tau') K_u^{(\mathrm{I})}(t) K_v^{(\mathrm{I})}(t - \tau') \hat{\sigma}(0) - C^*_{uv}(\tau') \hat{\sigma}(0) K_v^{(\mathrm{I})}(t - \tau') K_u^{(\mathrm{I})}(t) \right\}$$

next, we remember

$$|\psi(t)\rangle = e^{-iH_{\mathrm{S}}t/\hbar}|\tilde{\phi}(t)\rangle$$

and the fact that the reduced density operator $\hat{\rho}(t)$ which is related to the stochastic Schrödinger equation is defined by $|\psi(t)\rangle$; it follows

$$\hat{\rho}(t) = e^{-iH_{\mathrm{S}}t/\hbar}\hat{\sigma}(t)e^{-iH_{\mathrm{S}}t/\hbar}$$

we derive an equation for $\hat{\rho}(t)$

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[H_{\mathrm{S}}, \hat{\rho}(t)]_{-} + \int_0^t d\tau \sum_{u,v} \Big\{ C^*_{uv}(\tau)K_u U_{\mathrm{S}}(t)\hat{\sigma}(0)U^+_{\mathrm{S}}(t)K^{(\mathrm{I})}_v(-\tau)$$

$$+C_{uv}(\tau)K^{(\mathrm{I})}_v(\tau)U_{\mathrm{S}}(t)\hat{\sigma}(0)U^+_{\mathrm{S}}(t)K_u - C_{uv}(\tau)K_u K_v(-\tau)U_{\mathrm{S}}(t)\hat{\sigma}(0)U^+_{\mathrm{S}}(t) - C^*_{uv}(\tau)U_{\mathrm{S}}(t)\hat{\sigma}(0)U^+_{\mathrm{S}}(t)K^{(\mathrm{I})}_v(-\tau)K_u \Big\}$$

if in a consequent second–order theory the following identifcation is taken in the right–hand side of the foregoing equation

$$U_{\mathrm{S}}(t)\hat{\sigma}(0)U^+_{\mathrm{S}}(t) \approx \hat{\rho}(t)$$

we have obtained the standard quantum master equation