Redfield theory

$$H = H_s + \underbrace{H_b}_{\text{bath}} + \underbrace{V}_{\text{interaction}}$$

Focus on system observables.

Liouville equation of motion for density operator:

$$i\hbar \frac{\partial}{\partial t} \rho(t) = [H, \rho(t)]$$

Convert to the interaction representation using $H_0 = H_s + H_b$:

$$\rho^I(t) = e^{iH_0 t/\hbar} \rho(t) \, e^{-iH_0 t/\hbar}$$

This satisfies the equation

$$i\hbar \frac{\partial}{\partial t} \rho^I(t) = [V^I(t), \rho^I(t)]$$

where

$$V^I(t) = e^{iH_0 t/\hbar} \, V \, e^{-iH_0 t/\hbar}$$

Define a Liouville operator $L^I(t)$ such that

$$L^I(t) A \equiv [V^I(t), A]$$

for any A. $L^I(t)$ is a superoperator

Then

$$\boxed{i\hbar \frac{\partial}{\partial t} \rho^I(t) = L^I(t)\, \rho^I(t)}$$

Formal solution :

$$\rho^I(t) = \rho^I(0) - \frac{i}{\hbar} \int_0^t dt_1\, L^I(t_1)\, \rho^I(t_1)$$

Iterating,

$$\rho^I(t) = \rho^I(0) - \frac{i}{\hbar} \int_0^t dt_1\, L^I(t_1)\, \rho^I(0)$$
$$+ \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2\, L^I(t_1)\, L^I(t_2)\, \rho^I(0) + \cdots$$

Reduced density matrix :

$$\boxed{\tilde{\rho}^I(t) \equiv \mathrm{Tr}_b\, \rho^I(t)}$$

Assume factorized initial conditions :

$$\rho^I(0) = \rho_b(0)\, \rho_s(0)$$

with $\rho_b(0) = \dfrac{e^{-\beta H_b}}{\mathrm{Tr}_b\, e^{-\beta H_b}}$ canonical ensemble

i.e, $\tilde{\rho}^I(0) = \rho_s(0)$

$$\tilde{\rho}^I(t) = \tilde{\rho}^I(0) - \frac{i}{\hbar}\int_0^t dt_1 \, Tr_b\left\{ L^I(t_1)\rho_b(0)\right\}\rho_s(0)$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^t dt_2 \, Tr_b\left\{L^I(t_1)\, L^I(t_2)\,\rho_b(0)\right\}\rho_s(0)$$

$$+ \cdots$$

or $$\tilde{\rho}^I(t) = U(t)\,\tilde{\rho}^I(0) ,$$ where

$$U(t) = 1 - \frac{i}{\hbar}\int_0^t dt_1 \, Tr_b\left\{L^I(t_1)\rho_b(0)\right\}$$

$$+ \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \, Tr_b\left\{L^I(t_1)\,L^I(t_2)\,\rho_b(0)\right\} + \cdots$$

Taking time derivative,

$$\dot{\tilde{\rho}}^I(t) = \dot{U}(t)\,\tilde{\rho}^I(0) = \dot{U}(t)\,U^{-1}(t)\,\tilde{\rho}^I(t) \Rightarrow$$

$$\boxed{\dot{\tilde{\rho}}^I(t) = R(t)\,\tilde{\rho}^I(t)} ,$$ where

$$\boxed{R(t) \equiv \dot{U}(t)\,U^{-1}(t)}$$

Expressing in some basis $|\alpha\rangle$,

$$\boxed{\dot{\tilde{\rho}}^I_{\alpha\alpha'}(t) = \sum_{\beta\beta'} R_{\alpha\alpha';\beta\beta'}(t)\,\tilde{\rho}^I_{\beta\beta'}(t)}$$

Consider $U(t)$ up to second order in V :

$$U(t) \simeq 1 + M^{(1)}(t) + \frac{1}{2} M^{(2)}(t) .$$

$M^{(1)}(t)$ is zero because

$$\mathrm{Tr}_b \left[e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} , \rho_b \right] = \mathrm{Tr}_b \, e^{iH_0 t/\hbar} [V, \rho_b] \, e^{-iH_0 t/\hbar}$$

$$= e^{iH_s t/\hbar} \, \mathrm{Tr}_b \, e^{iH_b t/\hbar} [V, \rho_b] \, e^{-iH_b t/\hbar} \, e^{-iH_s t/\hbar}$$

$$= e^{iH_s t/\hbar} \sum_n e^{iE_n t/\hbar} \langle n | V\rho_b - \rho_b V | n \rangle \, e^{-iE_n t/\hbar} \, e^{-iH_s t/\hbar}$$

$$= e^{iH_s t/\hbar} \sum_n \left\{ \langle n|V|n\rangle \frac{e^{-\beta E_n}}{Z} - \frac{e^{-\beta E_n}}{Z} \langle n|V|n\rangle \right\} e^{-iH_s t/\hbar} = 0$$

Then $$U(t) \simeq 1 + \frac{1}{2} M^{(2)}(t)$$

$$R(t) \simeq \frac{\partial}{\partial t} \ln U(t) = \frac{1}{2} \frac{\partial}{\partial t} M^{(2)}(t)$$

$$= \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \, \mathrm{Tr}_b \left\{ L^I(t) \, L^I(t') \, \rho_b(0) \right\}$$

Use this in the equation for the reduced density matrix :

$$\dot{\tilde{\rho}}^{I}(t) = R(t) \cdot \tilde{\rho}^{I}(t) \qquad \Rightarrow$$

$$-\hbar^2 \dot{\tilde{\rho}}^{I}(t) = \int_0^t dt' \, Tr_b \left\{ L^I(t) \, L^I(t') \, \rho_b(0) \, \tilde{\rho}^I(t) \right\}$$

$$= \int_0^t dt' \, Tr_b \left\{ V^I(t) \, L^I(t') \, \rho_b(0) \, \tilde{\rho}^I(t) - L^I(t') \, \rho_b(0) \, \tilde{\rho}^I(t) \, V^I(t) \right\}$$

$$= \int_0^t dt' \, Tr_b \left\{ V^I(t) \, V^I(t') \, \rho_b(0) \, \tilde{\rho}^I(t) - V^I(t) \, \rho_b(0) \, \tilde{\rho}^I(t) \, V^I(t') \right.$$

$$\left. - V^I(t') \rho_b(0) \, \tilde{\rho}^I(t) V^I(t) + \rho_b(0) \, \tilde{\rho}^I(t) \, V^I(t) \, V^I(t') \right\}$$

Evaluate this in a basis $|\alpha\rangle$ for H_s :

Negative terms:

$$- \langle\alpha| \, Tr_b \left[V^I(t') \rho_b(0) \, \tilde{\rho}^I(t) \, V^I(t) \right] |\alpha'\rangle$$

$$= - Tr_b \sum_{\beta} \sum_{\beta'} V^I_{\alpha\beta}(t') \, \rho_b(0) \, \tilde{\rho}^I_{\beta\beta'}(t) \, V^I_{\beta'\alpha'}(t)$$

$$- \langle\alpha| \, Tr_b \left[V^I(t) \, \rho_b(0) \, \tilde{\rho}^I(t) \, V^I(t') \right] |\alpha'\rangle$$

$$= - Tr_b \sum_{\beta} \sum_{\beta'} V^I_{\alpha\beta}(t) \, \rho_b(0) \, \tilde{\rho}^I_{\beta\beta'}(t) \, V^I_{\beta'\alpha'}(t')$$

Positive terms :

First, $\quad \mathrm{Tr}_b\left[V^I(t)\, V^I(t')\, \rho_b(0)\, \tilde{\rho}^I(t) \right] = \mathrm{Tr}_b\left[\rho_b(0)\, \tilde{\rho}^I(t)\, V^I(t)\, V^I(t') \right]$

Proof: $\quad \mathrm{LHS} = \sum_{n,n'} \langle n | V^I(t)\, V^I(t') | n' \rangle \dfrac{e^{-\beta E_{n'}}}{Z} \langle n' | \tilde{\rho}^I(t) | n \rangle$

$\quad \mathrm{RHS} = \sum_{n,n'} \dfrac{e^{-\beta E_{n'}}}{Z} \langle n' | \tilde{\rho}^I(t) | n \rangle \langle n | V^I(t)\, V^I(t') | n' \rangle \quad \checkmark$

Then

$$\langle \alpha | \mathrm{Tr}_b\left[V^I(t)\, V^I(t')\, \rho_b(0)\, \tilde{\rho}^I(t) \right] | \alpha' \rangle$$

$$= \langle \alpha | \mathrm{Tr}_b\left[\rho_b(0)\, \tilde{\rho}^I(t)\, V^I(t)\, V^I(t') \right] | \alpha' \rangle$$

$$= \mathrm{Tr}_b \sum_{\beta'} \sum_{\gamma} \rho_b(0)\, \tilde{\rho}^I_{\alpha\beta'}(t)\, V^I_{\beta'\gamma}(t)\, V^I_{\gamma\alpha'}(t')$$

number,

Similarly, $\quad \mathrm{Tr}_b\left[\rho_b(0)\, \tilde{\rho}^I(t)\, V^I(t)\, V^I(t') \right] = \mathrm{Tr}_b\left[V^I(t')\, V^I(t)\, \rho_b(0)\, \tilde{\rho}^I(t) \right]$

and therefore

$$\langle \alpha | \mathrm{Tr}_b\left[\rho_b(0)\, \tilde{\rho}^I(t)\, V^I(t)\, V^I(t') \right] | \alpha' \rangle$$

$$= \mathrm{Tr}_b \sum_{\beta} \sum_{\gamma} V^I_{\alpha\gamma}(t')\, V^I_{\gamma\beta}(t)\, \rho_b(0)\, \tilde{\rho}^I_{\beta\alpha'}(t)$$

Therefore,

$$-\hbar^2 \dot{\tilde{\rho}}_{\alpha\alpha'}(t) = \int_0^t dt' \, \mathrm{Tr}_b \Big\{ \sum_\beta \sum_\gamma V^I_{\alpha\gamma}(t') \, V^I_{\gamma\beta}(t) \, \rho_b(0) \, \tilde{\rho}^I_{\beta\alpha'}(t)$$

$$+ \sum_{\beta'} \sum_\gamma \rho^I_{\alpha\beta'}(t) \, \rho_b(0) \, V^I_{\beta'\gamma}(t) \, V^I_{\gamma\alpha'}(t')$$

$$- \sum_\beta \sum_{\beta'} V^I_{\alpha\beta}(t) \, \rho_b(0) \, V^I_{\beta'\alpha'}(t') \, \tilde{\rho}^I_{\beta\beta'}(t)$$

$$- \sum_\beta \sum_{\beta'} V^I_{\alpha\beta}(t') \, \rho_b(0) \, V^I_{\beta'\alpha'}(t) \, \tilde{\rho}^I_{\beta\beta'}(t) \Big\}$$

Now define correlation functions

$$\boxed{\begin{aligned} G_{ijkl}(t-t') \equiv \mathrm{Tr}_b \Big\{ \rho_b(0) \, \langle l | \, e^{-iH_s t/\hbar} \, V^I(t) \, e^{iH_s t/\hbar} \, | k \rangle \\ \times \langle i | \, e^{-iH_s t'/\hbar} \, V^I(t') \, e^{iH_s t'/\hbar} \, | j \rangle \Big\} \end{aligned}}$$

i.e the coupling operators are now in the interaction representation only with respect to the bath.

Let the system eigenvalues be ϵ_n : $\quad H_s |n\rangle = \epsilon_n |n\rangle$.
Then

$$G_{ijkl}(t-t') = e^{-\frac{i}{\hbar}(\epsilon_l - \epsilon_k)t} \, e^{-\frac{i}{\hbar}(\epsilon_i - \epsilon_j)t'} \, \mathrm{Tr}_b \left[\rho_b(0) \, V^I_{lk}(t) \, V^I_{ij}(t') \right]$$

where $\quad V^I_{ij}(t) \equiv \langle i | V^I(t) | j \rangle$.

Then we have

$$\mathrm{Tr}_b\left[V^I_{\alpha\beta}(t)\, \rho_b(0)\, V^I_{\beta'\alpha'}(t') \right] = \mathrm{Tr}_b\left[\rho_b(0)\, V^I_{\beta'\alpha'}(t')\, V^I_{\alpha\beta}(t) \right]$$

$$= \exp\left\{ \frac{i}{\hbar}(\epsilon_{\beta'} - \epsilon_{\alpha'})t' + \frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta)t \right\} G_{\alpha\beta\,\alpha'\beta'}(t'-t) \; .$$

(The cyclic permutation of the trace was possible because $V^I_{\alpha\beta}$ etc are now operators only in the space of the bath.)

Then

$$\int_0^t dt' \; \mathrm{Tr}_b\left[V^I_{\alpha\beta}(t)\, \rho_b(0)\, V^I_{\beta'\alpha'}(t') \right]$$

$$= \int_0^t dt' \; e^{\frac{i}{\hbar}(\epsilon_{\beta'}-\epsilon_{\alpha'})t'} \, e^{\frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta)t} \, G_{\alpha\beta\alpha'\beta'}(t'-t) \qquad \text{set } t'-t = -t''$$

$$= \int_0^t dt' \; e^{\frac{i}{\hbar}(\epsilon_{\beta'}-\epsilon_{\alpha'})(t-t'')} \, e^{\frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta)t} \, G_{\alpha\beta\alpha'\beta'}(-t'')$$

$$= e^{\frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta-\epsilon_{\alpha'}+\epsilon_{\beta'})t} \int_0^t dt'' \; e^{\frac{i}{\hbar}(\epsilon_{\alpha'}-\epsilon_{\beta'})t''} \, G_{\alpha\beta\alpha'\beta'}(-t'')$$

Similarly,

$$\mathrm{Tr}_b\left[V^I_{\alpha\beta}(t')\, \rho_b(0)\, V^I_{\beta'\alpha'}(t) \right] = \exp\left\{ \frac{i}{\hbar}(\epsilon_{\beta'}-\epsilon_{\alpha'})t + \frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta)t' \right\} G_{\alpha\beta\alpha'\beta'}(t-t')$$

Then

$$\int_0^t dt' \, \mathrm{Tr}_b \left[V^I_{\alpha\beta}(t') \, \rho_b(0) \, V^I_{\beta\alpha'}(t) \right]$$

$$= \int_0^t dt' \, e^{\frac{i}{\hbar}(\epsilon_{\beta'} - \epsilon_{\alpha'})t} \, e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta)t'} \, G_{\alpha\beta\alpha'\beta'}(t-t') \qquad \text{set } t-t' = t''$$

$$= \int_0^t dt' \, e^{\frac{i}{\hbar}(\epsilon_{\beta'} - \epsilon_{\alpha'})t} \, e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta)(t-t'')} \, G_{\alpha\beta\alpha'\beta'}(t'')$$

$$= e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta - \epsilon_{\alpha'} + \epsilon_{\beta'})t} \int_0^t dt'' \, e^{\frac{i}{\hbar}(\epsilon_\beta - \epsilon_\alpha)t''} \, G_{\alpha\beta\alpha'\beta'}(t'')$$

$$\mathrm{Tr}_b \left[V^I_{\alpha\gamma}(t') \, V^I_{\gamma\beta}(t) \, \rho_b(0) \right. = \mathrm{Tr} \left[\rho_b(0) \, V^I_{\alpha\gamma}(t') \, V^I_{\gamma\beta}(t) \right]$$

$$= \exp \left[\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\gamma)t' + \frac{i}{\hbar}(\epsilon_\gamma - \epsilon_\beta)t \right] G_{\gamma\beta\gamma\alpha}(t'-t)$$

and by analogy

$$\int_0^t dt' \, \mathrm{Tr}_b \left[V^I_{\alpha\gamma}(t') \, V^I_{\gamma\beta}(t) \, \rho_b(0) \right]$$

$$= e^{\frac{i}{\hbar}(\epsilon_\gamma - \epsilon_\beta - \epsilon_\gamma + \epsilon_\alpha)t} \int_0^t dt'' \, e^{\frac{i}{\hbar}(\epsilon_\gamma - \epsilon_\alpha)t''} \, G_{\gamma\beta\gamma\alpha}(-t'')$$

$$= e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta - \epsilon_{\alpha'} + \epsilon_{\beta'})} \, \delta_{\alpha'\beta'} \int_0^t dt'' \, e^{\frac{i}{\hbar}(\epsilon_\gamma - \epsilon_\alpha)t''} \, G_{\gamma\beta\gamma\alpha}(-t'')$$

Finally, $\displaystyle\int_0^t dt' \, \mathrm{Tr}_b \left[\rho_b(0) \, V^I_{\beta'\gamma}(t) \, V^I_{\gamma\alpha'}(t') \right]$

$$= e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta - \epsilon_{\alpha'} + \epsilon_{\beta'})} \, \delta_{\alpha\beta} \int_0^t dt'' \, e^{\frac{i}{\hbar}(\epsilon_{\alpha'} - \epsilon_\gamma)t''} \, G_{\gamma\alpha'\gamma\beta'}(t'') \, .$$

Combining these results we find

$$\hbar^2 \dot{\tilde{\rho}}^{I}_{\alpha\alpha'}(t) = \sum_{\beta}\sum_{\beta'} e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta - \epsilon_{\alpha'} + \epsilon_{\beta'})t}$$

$$\times \int_0^t dt' \Big\{ -\sum_\gamma \Big[G_{\gamma\beta\gamma\alpha}(-t')\, e^{i\omega_{\gamma\alpha}t'}\, \delta_{\alpha'\beta'} + G_{\gamma\alpha'\gamma\beta'}(t')\, e^{i\omega_{\alpha'\gamma}t'}\, \delta_{\alpha\beta} \Big]$$

$$+ G_{\alpha\beta\alpha'\beta'}(-t')\, e^{i\omega_{\alpha'\beta'}t'} + G_{\alpha\beta\alpha'\beta'}(t')\, e^{i\omega_{\beta\alpha}t'} \Big\} \tilde{\rho}^{I}_{\beta\beta'}(t)$$

If we assume that the correlation functions are symmetric we get

$$\hbar^2 \dot{\tilde{\rho}}^{I}_{\alpha\alpha'}(t) = \sum_{\beta}\sum_{\beta'} e^{\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta - \epsilon_{\alpha'} + \epsilon_{\beta'})t}$$

$$\times \int_0^t dt' \Big\{ -\sum_\gamma G_{\gamma\beta\gamma\alpha}(t')\, e^{i\omega_{\gamma\alpha}t'}\, \delta_{\alpha'\beta'} - \sum_\gamma G_{\gamma\alpha'\gamma\beta'}(t')\, e^{i\omega_{\alpha'\gamma}t'}\, \delta_{\alpha\beta}$$

$$+ G_{\alpha\beta\alpha'\beta'}(t')\, e^{i\omega_{\alpha'\beta'}t'} + G_{\alpha\beta\alpha'\beta'}(t')\, e^{i\omega_{\beta\alpha}t'} \Big\} \tilde{\rho}^{I}_{\beta\beta'}(t)$$

Now we assume that the correlation functions decay to zero within some time τ_c. (This is generally true if the bath is macroscopic.) Then for $t \gg \tau_c$ we can extend the limit of integration to ∞.

Defining spectral densities

$$\boxed{J_{\alpha\alpha'\beta\beta'}(\omega) \equiv \int_0^\infty dt'\; e^{i\omega t'}\; G_{\alpha\alpha'\beta\beta'}(t')}$$

we can rewrite the equation for $\dot{\tilde{\rho}}_{\alpha\alpha'}$ in the following form:

$$\boxed{\dot{\tilde{\rho}}^{I}_{\alpha\alpha'}(t) = \sum_{\beta}\sum_{\beta'} e^{\frac{i}{\hbar}(\epsilon_{\alpha}-\epsilon_{\beta}-\epsilon_{\alpha'}+\epsilon_{\beta'})t} \; R_{\alpha\alpha';\beta\beta'} \; \tilde{\rho}^{I}_{\beta\beta'}(t)}$$

Redfield equations

where

$$\boxed{\begin{aligned} R_{\alpha\alpha';\beta\beta'} \equiv \frac{1}{\hbar^2}\Big\{ & J_{\alpha\beta\alpha'\beta'}(\omega_{\alpha'\beta'}) + J_{\alpha\beta\alpha'\beta'}(\omega_{\beta\alpha}) \\ & - \sum_{\gamma} J_{\gamma\beta\gamma\alpha}(\omega_{\gamma\alpha})\,\delta_{\alpha'\beta'} - \sum_{\gamma} J_{\gamma\alpha'\gamma\beta'}(\omega_{\alpha'\gamma})\,\delta_{\alpha\beta}\Big\} \end{aligned}}$$

Redfield relaxation matrix

References:

- A.G. Redfield, Adv. Magn. Reson. 1, 1 (1966)
- B. Laird, J. Budimir and J.L. Skinner, J. Chem. Phys. 94, 4391 (1991)

Application to a two-level system

In the basis of eigenstates $|0\rangle$ and $|1\rangle$, the free TLS Hamiltonian is

$$H_s = E_1 |1\rangle\langle 1| \qquad (E_0 \equiv 0).$$

Harmonic bath: $$H_b = \sum_k \frac{P_k^2}{2m} + \frac{1}{2} m\omega_k^2 Q_k^2 = \sum_k (\hbar\omega_k)(a_k^\dagger a_k + \tfrac{1}{2})$$

Coupling: $$V = \sum_k c_k Q_k \left(|0\rangle\langle 1| + |1\rangle\langle 0| \right)$$

Recall definition of correlation functions

$$G_{\alpha\alpha'\beta\beta'}(t-t') = \mathrm{Tr}_b \Big\{ \rho_b(0) \langle \beta' | e^{iH_b t/\hbar} V e^{-iH_b t/\hbar} | \beta \rangle \times \langle \alpha | e^{iH_b t'/\hbar} V e^{-iH_b t'/\hbar} | \alpha' \rangle \Big\}$$

For the spin-boson Hamiltonian this becomes

$$G_{\alpha\alpha'\beta\beta'}(t-t') = \mathrm{Tr}_b \Big[\rho_b(0)\, e^{iH_b t/\hbar} \sum_k c_k Q_k \langle \beta' | \left(|0\rangle\langle 1| + |1\rangle\langle 0| \right) | \beta' \rangle \times e^{-iH_b (t-t')/\hbar} \sum_{k'} c_{k'} Q_{k'} \langle \alpha | \left(|0\rangle\langle 1| + |1\rangle\langle 0| \right) | \alpha' \rangle\, e^{-iH_b t'/\hbar} \Big]$$

This is nonzero only if $\alpha + \alpha' = \beta + \beta' = 1$.

Therefore the relaxation matrix will have some terms equal to zero.

Specifically, the symmetry of the problem implies that the Redfield equations will have the following form:

$$\dot{\tilde{\rho}}^{I}_{00}(t) = R_{0000}\,\tilde{\rho}^{I}_{00}(t) + R_{0011}\,\tilde{\rho}^{I}_{11}(t)$$

$$\dot{\tilde{\rho}}^{I}_{11}(t) = R_{1100}\,\tilde{\rho}^{I}_{00}(t) + R_{1111}\,\tilde{\rho}^{I}_{11}(t)$$

$$\dot{\tilde{\rho}}^{I}_{01}(t) = R_{0101}\,\tilde{\rho}^{I}_{01}(t) + R_{0110}\,\tilde{\rho}^{I}_{10}(t)$$

$$\dot{\tilde{\rho}}^{I}_{10}(t) = R_{1001}\,\tilde{\rho}^{I}_{01}(t) + R_{1010}\,\tilde{\rho}^{I}_{10}(t)$$

Converting to the Schrödinger representation leaves the equations for the diagonal terms unchanged, while those of the off-diagonal terms get modified by the addition of frequency factors $\pm i\omega_{10}$. ($\omega_{10} \equiv E_1/\hbar$).

Notice that since

$$\tilde{\rho}_{00}(t) + \tilde{\rho}_{11}(t) = 1 \quad \Rightarrow \quad \dot{\tilde{\rho}}_{00} + \dot{\tilde{\rho}}_{11} = 0 \quad \Rightarrow$$

$$(R_{0000} + R_{1100})\,\tilde{\rho}_{00}(t) + (R_{0011} + R_{1111})\,\underbrace{\tilde{\rho}_{11}(t)}_{1-\tilde{\rho}_{00}(t)} = 0$$

$$\Rightarrow \quad R_{0000} + R_{1100} - R_{0011} - R_{1111} = 0 \quad \text{and} \quad R_{0011} + R_{1111} = 0 \quad \Rightarrow$$

$-R_{1111} = \boxed{R_{0011} \equiv k_{01}}$ and $-R_{0000} = \boxed{R_{1100} \equiv k_{10}}$

So we have

$$\boxed{\begin{aligned} \dot{\tilde{\rho}}_{00}(t) &= -k_{10}\,\tilde{\rho}_{00}(t) + k_{01}\,\tilde{\rho}_{11}(t) \\ \dot{\tilde{\rho}}_{11}(t) &= k_{10}\,\tilde{\rho}_{00}(t) - k_{01}\,\tilde{\rho}_{11}(t) \end{aligned}}$$

Calculation of rate constants:

We cannot use the final form of the relaxation matrix, because the correlation functions are not symmetric in the case of a quantum mechanical bath

Going back to the unsymmetrized form and taking $t \to \infty$,

$$\hbar^2 R_{0000} = \int_0^\infty dt' \left\{ - \left[G_{1010}(-t')\, e^{i\omega_{10}t'} + c.c. \right] \right\}$$

$$= -2\,\mathrm{Re} \int_0^\infty dt'\, \mathrm{Tr}_b \left\{ \rho_b(0)\, e^{iH_b(-t')/\hbar} \sum_k c_k Q_k\, e^{-iH_b(-t')/\hbar} \sum_{k'} c_{k'} Q_{k'} \right\} e^{i\omega_{10}t'}$$

Define the bath correlation function

$$C(t) \equiv \mathrm{Tr}_b \left\{ \rho_b(0) \left[e^{iH_b t/\hbar} \sum_k c_k Q_k \, e^{-iH_b t/\hbar} \right] \sum_{k'} c_{k'} Q_{k'} \right\}$$

$$= \mathrm{Tr}_b \left\{ \rho_b(0) \, \Lambda(t) \, \Lambda(0) \right\}$$

where $$\Lambda(t) \equiv e^{iH_b t/\hbar} \sum_k c_k Q_k \, e^{-iH_b t/\hbar}$$

Then

$$R_{0000} = -\frac{2}{\hbar^2} \mathrm{Re} \int_0^\infty dt \; C^*(t) \, e^{iE_1 t/\hbar}$$

$$= -\frac{2}{\hbar^2} \mathrm{Re} \int_0^\infty dt \; C(t) \, e^{-iE_1 t/\hbar}$$

Define the Fourier transform

$$\hat{C}(\omega) = \int_{-\infty}^{\infty} dt \; e^{i\omega t} \, C(t)$$

with inverse $$C(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \; e^{-i\omega t} \, \hat{C}(\omega)$$

Then

$$R_{0000} = -\frac{1}{\hbar^2} \mathrm{Re} \, \hat{C}\left(-\frac{E_1}{\hbar}\right)$$

and $$k_{10} = \frac{1}{\hbar^2} \mathrm{Re} \, \hat{C}\left(-\frac{E_1}{\hbar}\right)$$

It is easy to show that $$C(t) = \sum_k \frac{\hbar c_k^2}{2m\omega_k} \left[\coth(\hbar\omega_k \beta) \cos\omega_k t - i \sin\omega_k t \right]$$

Defining the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_k \frac{C_k^2}{m\omega_k} \delta(\omega-\omega_k)$$

and replacing ω_k by $\pm\omega$ by virtue of the δ functions, we have

$$\hat{C}(\omega) = 2\pi \sum_k \frac{\hbar c_k^2}{2m\omega_k} \left[\frac{e^{\hbar\omega\beta}}{e^{\hbar\omega\beta}-1} \delta(\omega-\omega_k) + \frac{1}{e^{-\hbar\omega\beta}-1} \delta(\omega+\omega_k) \right]$$

$$= 2\hbar \left\{ J(\omega) \frac{\exp(\hbar\omega\beta)}{\exp(\hbar\omega\beta)-1} + J(-\omega) \frac{1}{\exp(-\hbar\omega\beta)-1} \right\}$$

Since $J(\omega) = 0$ for $\omega = -E_1/\hbar$ $\Rightarrow$

$$\boxed{k_{10} = \frac{2}{\hbar} \frac{1}{e^{\beta E_1}-1} J\left(\frac{E_1}{\hbar}\right)}$$

Similarly,

$$\boxed{k_{01} = \frac{2}{\hbar} \frac{e^{\beta E_1}}{e^{\beta E_1}-1} J\left(\frac{E_1}{\hbar}\right)}$$

and the rate constants satisfy detailed balance,

$$\boxed{\frac{k_{10}}{k_{01}} = e^{-\beta E_1}} .$$

Off-diagonal elements:

$$\dot{\tilde{\rho}}_{10}(t) = -\left[i\left(\frac{E_1}{\hbar} + \Delta\omega \right) + \frac{1}{\tau_2} \right] \tilde{\rho}_{10}(t) + \cdots$$

$$\dot{\tilde{\rho}}_{01}(t) = \left[i\left(\frac{E_1}{\hbar} + \Delta\omega \right) - \frac{1}{\tau_2} \right] \tilde{\rho}_{01}(t) + \cdots$$

small terms

Population relaxation:

$\tilde{\rho}_{11}(t)$ relaxes to equilibrium with decay rate $k_{10} + k_{01} \equiv 1/\tau_1$

$$\frac{1}{\tau_2} = \frac{1}{2\tau_1} + \frac{1}{\tau_2'}$$

"pure dephasing"

$$\Rightarrow \quad \frac{1}{\tau_2} \geqslant \frac{1}{2\tau_1} \qquad \text{(through 2nd order)}$$