5 Three Level System with Sequential Coupling

we discuss a three level system $a = 1, 2, 3$ with a coupling Φ_{12} connecting the first to the second level and a coupling Φ_{23} which relates the second to the third level;
this sequential type of coupling initiates transfer from the first to the third level exclusively via the second level;
the rate from the first to the third state is constituted by six different terms corresponding to the arrangement VVW_aVV;
they are pairwise complex conjugated;
the three different terms if included into the trace expression are labeled by the number of the paths (see respective figure)

$$C_{31}(t_3, t_2, t_1) = C_{31}^{(\mathrm{I})}(t_3, t_2, t_1) + C_{31}^{(\mathrm{II})}(t_3, t_2, t_1) + C_{31}^{(\mathrm{III})}(t_3, t_2, t_1)$$

the different parts read in detail

$$C_{31}^{(\mathrm{I})}(t_3, t_2, t_1) = \frac{1}{\hbar^4}\mathrm{tr}_{\mathrm{R}}\{\langle 3|U(t_3 + t_2)\hat{V}U(t_1)\hat{V}\hat{W}_1U^+(t_1 + t_2)\hat{V}U^+(t_3)\hat{V}|3\rangle\}$$

$$C_{31}^{(\mathrm{II})}(t_3, t_2, t_1) = \frac{1}{\hbar^4}\mathrm{tr}_{\mathrm{R}}\{\langle 3|U(t_3)\hat{V}U(t_2 + t_1)\hat{V}\hat{W}_1U^+(t_1)\hat{V}U^+(t_2 + t_3)\hat{V}|3\rangle\}$$

$$C_{31}^{(\mathrm{III})}(t_3, t_2, t_1) = \frac{1}{\hbar^4}\mathrm{tr}_{\mathrm{R}}\{\langle 3|\hat{V}U(t_3 + t_2 + t_1)\hat{V}\hat{W}_1U^+(t_1)\hat{V}U^+(t_2)\hat{V}U^+(t_3)|3\rangle\}$$

we specify $\hat{V}$ and obtain

$$C_{31}^{(I)}(t_3,t_2,t_1) = \frac{1}{\hbar^4}\mathrm{tr_R}\{U_3(t_3+t_2)\Phi_{32}U_2(t_1)\Phi_{21}\hat{R}_1U_1^+(t_1+t_2)\Phi_{12}U_2^+(t_3)\Phi_{23}\}$$
$$= \frac{1}{\hbar^4}\mathrm{tr_R}\{\hat{R}_1U_1^+(t_1+t_2)\Phi_{12}U_2^+(t_3)\Phi_{23}U_3(t_3+t_2)\Phi_{32}U_2(t_1)\Phi_{21}\}$$

$$C_{31}^{(II)}(t_3,t_2,t_1) = \frac{1}{\hbar^4}\mathrm{tr_R}\{U_3(t_3)\Phi_{32}U_2(t_2+t_1)\Phi_{21}\hat{R}_1U_1^+(t_1)\Phi_{12}U_2^+(t_2+t_3)\Phi_{23}\}$$
$$= \frac{1}{\hbar^4}\mathrm{tr_R}\{\hat{R}_1U_1^+(t_1)\Phi_{12}U_2^+(t_2+t_3)\Phi_{23}U_3(t_3)\Phi_{32}U_2(t_2+t_1)\Phi_{21}\}$$

$$C_{31}^{(III)}(t_3,t_2,t_1) = \frac{1}{\hbar^4}\mathrm{tr_R}\{\Phi_{32}U_2(t_3+t_2+t_1)\Phi_{21}\hat{R}_1U_1^+(t_1)\Phi_{12}U_2^+(t_2)\Phi_{23}U_3^+(t_3)\}$$
$$= \frac{1}{\hbar^4}\mathrm{tr_R}\{\hat{R}_1U_1^+(t_1)\Phi_{12}U_2^+(t_2)\Phi_{23}U_3^+(t_3)\Phi_{32}U_2(t_3+t_2+t_1)\Phi_{21}\}$$

in order to take a closer look at the fourth-order rate expression we consider a simple example where only the discrete energies $\hbar\omega_a$ ($a=1,2,3$) contribute and a respective reservoir coordinate dependence is neglected (the Hamiltonians H_a are replaced by $\hbar\omega_a$);

$$C_{31}^{(\mathrm{I})}(t_3, t_2, t_1) = \frac{|\Phi_{12}\Phi_{23}|^2}{\hbar^4} \exp\left(i\omega_{12}t_1 + i\omega_{13}t_2 + i\omega_{23}t_3\right)$$

$$C_{31}^{(\mathrm{II})}(t_3, t_2, t_1) = \frac{|\Phi_{12}\Phi_{23}|^2}{\hbar^4} \exp\left(i\omega_{12}t_1 + i\omega_{23}t_3\right)$$

$$C_{31}^{(\mathrm{III})}(t_3, t_2, t_1) = \frac{|\Phi_{12}\Phi_{23}|^2}{\hbar^4} \exp\left(i\omega_{12}t_1 + i\omega_{32}t_3\right)$$

be aware of the fact that $C_{31}^{(\mathrm{I})}$ depends on t_2 but $C_{31}^{(\mathrm{II})}$ as well as $C_{31}^{(\mathrm{III})}$ do not;
this indicates a possible factorization in a t_1–dependent and a t_3–dependent part, and a resulting compensation by the product of two second–order correlation functions;
it can be also interpreted as a transition from level 1 to level 3, but interrupted by level 2 (the extent of this interruption depends on the used model);

the respective approximation for the second–order rate takes the form ($\tilde{\omega} = \omega + i\varepsilon$)

$$K_{ba}^{(2)}(\omega) = -\frac{|\Phi_{ab}|^2}{\hbar^2}\left(\frac{i}{\tilde{\omega} + \omega_{ab}} + \frac{i}{\tilde{\omega} - \omega_{ab}}\right)$$

we get the fourth order expression as

$$K_{31}^{(4)}(\omega) = L_{31}^{(4)}(\omega) - \frac{i}{\tilde{\omega}} K_{32}^{(2)}(\omega) K_{21}^{(2)}(\omega)$$

$$= -i \frac{|\Phi_{12}\Phi_{23}|^2}{\hbar^4} \Big(\frac{1}{(\tilde{\omega}+\omega_{12})(\tilde{\omega}+\omega_{13})(\tilde{\omega}+\omega_{23})} + \frac{1}{(\tilde{\omega}-\omega_{12})(\tilde{\omega}-\omega_{13})(\tilde{\omega}-\omega_{23})}$$

$$+ \frac{1}{(\tilde{\omega}+\omega_{12})\tilde{\omega}(\tilde{\omega}+\omega_{23})} + \frac{1}{(\tilde{\omega}-\omega_{12})\tilde{\omega}(\tilde{\omega}-\omega_{23})} + \frac{1}{(\tilde{\omega}+\omega_{12})\tilde{\omega}(\tilde{\omega}+\omega_{32})} + \frac{1}{(\tilde{\omega}-\omega_{12})\tilde{\omega}(\tilde{\omega}-\omega_{32})}$$

$$- \frac{1}{\tilde{\omega}} \Big[\frac{1}{\tilde{\omega}-\omega_{23}} + \frac{1}{\tilde{\omega}+\omega_{23}} \Big] \Big[\frac{1}{\tilde{\omega}-\omega_{12}} + \frac{1}{\tilde{\omega}+\omega_{12}} \Big] \Big)$$

only the first two terms contribute (corresponding to the first Liouville space pathway I);
the fourth–order rate due to pathways II and III is completely compensated by the factorized part of the rate;
we obtain the ordinary rate expression as:

$$k_{1\to 3}^{(4)} = \frac{2|\Phi_{12}\Phi_{23}|^2}{\hbar^4} \mathrm{Im} \Big(\frac{1}{(\omega_{12}+i\varepsilon)(\omega_{13}+i\varepsilon)(\omega_{23}+i\varepsilon)} \Big)$$

$$= \frac{2\pi|\Phi_{12}\Phi_{23}|^2}{\hbar^4} \Big(\frac{\delta(\omega_{13})}{\varepsilon_{12}^2} - \frac{\delta(\omega_{23})}{\varepsilon_{12}^2} - \frac{\delta(\omega_{12})}{\varepsilon_{23}^2} + \pi^2 \delta(\omega_{13})\delta(\omega_{23})\delta(\omega_{12}) \Big)$$

we assume that $\omega_{12} \neq 0$ and $\omega_{32} \neq 0$ and arrive at

$$k^{(4)}_{1\to 3} = \frac{2\pi}{\hbar} \left| \frac{\Phi_{12}\Phi_{23}}{\hbar\omega_{12}} \right|^2 \delta(\hbar\omega_{13})$$

this is standard formula used whenever transfer processes are studied which are mediated by an intermediate (bridge level);
the present discussion demonstrates, however, that the intermediate level has to be off–resonant to the initial and final level;
if this is not the case the more general expression has to be used;