11 Feb 98

Redfield Relaxation Questions

- why does Pollard & Friesner's method save time & effort – can we reformulate it in terms of the Redfield tensor itself?
- how does temperature affect energy-dissipation and dephasing rates?
- does Redfield theory work the same way with a non-Hermitian "density matrix"?
- what is pure dephasing?
- Check Lowell's Eq. (21)
- how do coherences affect the energy dissipation rate?
- what is incoherent dissipation?
- is super-radiant emission a correct description?
- markovian approx'n in interaction v. Schrödinger rep – how does this issue connect with our assumption that bath relaxation is rapid compared with system bohr frequencies?

$$H = H_s + H_b + V$$

$\uparrow$ system-bath interaction

$$i\frac{d\rho}{dt} = [H,\rho] \equiv \mathcal{L}\rho \qquad \text{where } \mathcal{L} = \mathcal{L}_s + \mathcal{L}_b + \mathcal{L}_v$$

$$\mathcal{P}A \equiv \rho_b \, \mathrm{Tr}_b A \qquad \text{where } \rho_b = \frac{e^{-\beta H_b}}{Z_b}$$

$$Q \equiv 1 - \mathcal{P}$$

$$i\frac{d\mathcal{P}\rho}{dt} = \mathcal{P}\mathcal{L}\mathcal{P}\rho + \mathcal{P}\mathcal{L}Q\rho$$

$$i\frac{dQ\rho}{dt} = Q\mathcal{L}\mathcal{P}\rho + Q\mathcal{L}Q\rho \Rightarrow i\frac{d}{dt}\left(e^{iQ\mathcal{L}Qt}Q\rho\right) = e^{itQ\mathcal{L}Q}Q\mathcal{L}\mathcal{P}\rho$$

formal soln: $e^{iQ\mathcal{L}Qt}Q\rho(t) = Q\rho(0) - i\int_0^t d\tau\, e^{i\tau Q\mathcal{L}Q}Q\mathcal{L}\mathcal{P}\rho(\tau)$

$$\boxed{Q\rho(t) = e^{-itQ\mathcal{L}}Q\rho(0) - i\int_0^t d\tau\, e^{-i(t-\tau)Q\mathcal{L}}Q\mathcal{L}\mathcal{P}\rho(\tau)}$$

OK to here

substitution gives a closed integro-differential equation for $\mathcal{P}\rho(t)$:

$$i\frac{d\mathcal{P}\rho(t)}{dt} = \mathcal{P}\mathcal{L}\mathcal{P}\rho(t) + \mathcal{P}\mathcal{L}\, e^{-itQ\mathcal{L}}Q\rho(0) - i\int_0^t d\tau\, \mathcal{P}\mathcal{L}\, e^{-i(t-\tau)Q\mathcal{L}}Q\mathcal{L}\mathcal{P}\rho(\tau)$$

$$\mathcal{P}\mathcal{L}\mathcal{P} A = \rho_b \mathrm{Tr}_b[(\mathcal{L}_s + \cancel{\mathcal{L}_b} + \mathcal{L}_v)\, \rho_b \mathrm{Tr}_b A]$$

$$= \rho_b \underbrace{(\mathrm{Tr}_b \rho_b)}_{1} \mathcal{L}_s \mathrm{Tr}_b A + \rho_b \mathrm{Tr}_b [V, \rho_b \mathrm{Tr}_b A]$$

$$= \mathcal{P}\mathcal{L}_s A + \rho_b [\langle V \rangle, \mathrm{Tr}_b A]$$

$$\boxed{\mathcal{P}\mathcal{L}\mathcal{P} = \mathcal{P}\mathcal{L}_s}$$

$$= \mathcal{L}_s \mathcal{P}$$

if we set things up with

$$\langle V \rangle \equiv \mathrm{Tr}_b \rho_b V = 0$$

[we can easily do this: if $\langle V_{old} \rangle \neq 0$, write

$$V_{old} = \underbrace{V_{old} - \langle V_{old} \rangle}_{\text{call this } V_{new}} + \langle V_{old} \rangle$$

and incorporate this system operator in H_s.]

$$\mathcal{P}\mathcal{L}_s \mathcal{Q} A = \rho_b \mathrm{Tr}_b \mathcal{L}_s A - \rho_b \mathrm{Tr}_b \mathcal{L}_s \rho_b \mathrm{Tr}_b A$$

$$= \rho_b \mathcal{L}_s \mathrm{Tr}_b A - \rho_b (\mathrm{Tr}_b \rho_b) \mathcal{L}_s \mathrm{Tr}_b A = 0$$

$$\mathcal{P}\mathcal{L}_b \mathcal{Q} A = \rho_b \mathrm{Tr}_b [H_b, \mathcal{Q} A] = 0$$

$$\boxed{\mathcal{P}\mathcal{L}\mathcal{Q} = \mathcal{P}\mathcal{L}_v \mathcal{Q}}$$

$$Q\mathcal{L}\mathcal{P}A = \mathcal{L}\mathcal{P}A - \mathcal{P}\mathcal{L}\mathcal{P}A \underset{\substack{\uparrow \\ \text{see above, p. 3}}}{=} \mathcal{L}\mathcal{P}A - \mathcal{L}_s\mathcal{P}A$$

$$= \underbrace{\mathcal{L}_b\mathcal{P}A}_{0} + \mathcal{L}_v\mathcal{P}A \Longrightarrow \boxed{Q\mathcal{L}\mathcal{P} = \mathcal{L}_v\mathcal{P}}$$

$$\boxed{\begin{aligned} i\frac{d\mathcal{P}\rho(t)}{dt} &= \mathcal{L}_s\mathcal{P}\rho(t) + \mathcal{P}\mathcal{L}_v e^{-itQ\mathcal{L}} Q\rho(0) \\ &\quad - i\int_0^t d\tau\, \mathcal{P}\mathcal{L}_v e^{-i(t-\tau)Q\mathcal{L}} \mathcal{L}_v\mathcal{P}\rho(\tau) \end{aligned}}$$

Can we do anything with the $Q\rho(0)$ term?

$$i\frac{d}{dt} e^{-itQ\mathcal{L}} = Q\mathcal{L}\, e^{-itQ\mathcal{L}}$$

$$i\frac{d}{dt} e^{itQ(\mathcal{L}_s+\mathcal{L}_b)} e^{-itQ\mathcal{L}} = e^{itQ(\mathcal{L}_s+\mathcal{L}_b)} \left(-Q(\mathcal{L}_s+\mathcal{L}_b) + Q\mathcal{L}\right) e^{-itQ\mathcal{L}}$$

$$= e^{itQ(\mathcal{L}_s+\mathcal{L}_b)} Q\mathcal{L}_v\, e^{-itQ\mathcal{L}}$$

$$e^{itQ(\mathcal{L}_s+\mathcal{L}_b)} e^{-itQ\mathcal{L}} = 1 - i\int_0^t d\tau\, e^{i\tau Q(\mathcal{L}_s+\mathcal{L}_b)} Q\mathcal{L}_v\, e^{-i\tau Q\mathcal{L}}$$

$$\boxed{e^{-itQ\mathcal{L}} = e^{-itQ(\mathcal{L}_s+\mathcal{L}_b)} - i\int_0^t d\tau\, e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)} Q\mathcal{L}_v\, e^{-i\tau Q\mathcal{L}}}$$

$$i\frac{d\mathcal{P}\rho(t)}{dt} = \mathcal{L}_s\mathcal{P}\rho(t) + \mathcal{P}\mathcal{L}_v\, e^{-itQ(\mathcal{L}_s+\mathcal{L}_b)}Q\rho(0)$$

$$-i\int_0^t d\tau\, \mathcal{P}\mathcal{L}_v\, e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)}Q\mathcal{L}_v\, e^{-i\tau Q\mathcal{L}}Q\rho(0)$$

$$-i\int_0^t d\tau\, \mathcal{P}\mathcal{L}_v\, e^{-i(t-\tau)Q\mathcal{L}}\mathcal{L}_v\mathcal{P}\rho(\tau)$$

we assume (and will check later) that τ must be near both t & zero in the first integral and near t in the second integral. This assumption* motivates a WEAK COUPLING APPROXIMATION according to which $e^{-i\tau Q\mathcal{L}} \cong e^{-i\tau Q(\mathcal{L}_s+\mathcal{L}_b)}$ in the first integrand and $e^{-i(t-\tau)Q\mathcal{L}} \cong e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)}$ in the second.

$$\boxed{\begin{aligned} i\frac{d\mathcal{P}\rho(t)}{dt} \cong{}& \mathcal{L}_s\mathcal{P}\rho(t) + \mathcal{P}\mathcal{L}_v\, e^{-itQ(\mathcal{L}_s+\mathcal{L}_b)}Q\rho(0)\\ &-i\int_0^t d\tau\, \mathcal{P}\mathcal{L}_v\, e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)}Q\mathcal{L}_v\, e^{-i\tau Q(\mathcal{L}_s+\mathcal{L}_b)}Q\rho(0)\\ &-i\int_0^t d\tau\, \mathcal{P}\mathcal{L}_v\, e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)}\mathcal{L}_v\mathcal{P}\rho(\tau)\end{aligned}}$$

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* This assumption is unjustified so far: We've specified the form of ρ_b, but not of $\mathcal{L}$ nor $\rho(0)$!

Things get markedly simpler looking if we specialize to the situation $Q\rho(0) = 0$:

$$i\frac{d\mathcal{P}\rho(t)}{dt} = \mathcal{L}_s \mathcal{P}\rho(t) - i\int_0^t d\tau\, \mathcal{P}\mathcal{L}_v\, e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)}\, \mathcal{L}_v \mathcal{P}\rho(\tau)$$

we define the REDUCED DENSITY MATRIX of the system as

$\sigma(t) \equiv \mathrm{Tr}_b\, \rho(t)$. Then $\mathcal{P}\rho(t) = \rho_b\, \sigma(t)$, and

> NOTE ALSO:
> $Q\rho(0) = \rho(0) - \rho_b\sigma(0) = 0$
> which implies
> $\rho(0) = \rho_b\sigma(0)$

$$i\frac{d\sigma(t)}{dt} = \mathcal{L}_s\sigma(t) - i\int_0^t d\tau\, \mathrm{Tr}_b\!\left(\mathcal{L}_v\, e^{-i(t-\tau)Q(\mathcal{L}_s+\mathcal{L}_b)}\, \mathcal{L}_v\rho_b\right)\sigma(\tau)$$

$$= \mathcal{L}_s\sigma(t) - i\int_0^t d\tau\, K(t-\tau)\,\sigma(\tau)$$

$$\tau' = t-\tau \;\Rightarrow\; \tau = t-\tau' \qquad d\tau = -d\tau'$$

$$\boxed{i\frac{d\sigma(t)}{dt} = \mathcal{L}_s\sigma(t) - i\int_0^t d\tau\, K(\tau)\,\sigma(t-\tau)}$$

$$\boxed{\text{where}\quad K(\tau) \equiv \mathrm{Tr}_b\!\left(\mathcal{L}_v\, e^{-i\tau Q(\mathcal{L}_s+\mathcal{L}_b)}\, \mathcal{L}_v\rho_b\right)}$$

for confirmation of agreement w/ 16 May 94 see p. (a)

is the RELAXATION SUPEROPERATOR

On pp. b–d it's shown that the Q in the exponent is superfluous:

$$\boxed{K(\tau) = \mathrm{Tr}_b\!\left(\mathcal{L}_v\, e^{-i\tau(\mathcal{L}_s+\mathcal{L}_b)}\, \mathcal{L}_v\rho_b\right)}$$

In the interaction picture $\tilde{\sigma}(t) = e^{i\mathcal{L}_s t}\sigma(t)$

$$i\frac{d\tilde{\sigma}(t)}{dt} = -i\int_0^t d\tau\; e^{i\mathcal{L}_s t} K(\tau)\, \underbrace{\sigma(t-\tau)}_{e^{-i\mathcal{L}_s(t-\tau)}\tilde{\sigma}(t-\tau)}$$

$$i\frac{d\tilde{\sigma}(t)}{dt} = -i\int_0^t d\tau\; e^{i\mathcal{L}_s t} K(\tau)\, e^{-i\mathcal{L}_s(t-\tau)}\,\tilde{\sigma}(t-\tau)$$

we now replace $\tilde{\sigma}(t-\tau)$ by $\tilde{\sigma}(t)$ on the assumption

that $K(\tau)e^{i\tau\mathcal{L}_s}$ decays rapidly compared with the rate of change of $\tilde{\sigma}$. As there are no bohr oscillations in the interaction picture, changes in $\tilde{\sigma}$ are due to popalation relaxation and dephasing only. This MARKOVIAN APPROXIMATION is obviously favored by weak coupling.

$$\frac{d\tilde{\sigma}(t)}{dt} \cong -\int_0^t d\tau\; e^{i\mathcal{L}_s t} K(\tau)\, e^{i\tau\mathcal{L}_s}\, e^{-it\mathcal{L}_s}\,\tilde{\sigma}(t)$$

once t exceeds the "bath relaxation time" τ_r (decay time of $K(\tau)e^{i\tau\mathcal{L}_s}$) the upper integration limit can be replaced by ∞.

Making this same replacement right from the start introduces an initial "slippage" error,

$$\Delta\sigma_{\text{slippage}} \sim -\tau_{rel} \int_0^\infty d\tau \; K(\tau)\, e^{i\tau\mathcal{L}_s} \; \sigma(0) \quad ,$$

in the reduced density matrix (Schrödinger picture). By the weak coupling assumption, this is a small mistake, so we finally arrive at

$$\boxed{\frac{d\bar{\sigma}(t)}{dt} = -\int_0^\infty d\tau \; e^{i\mathcal{L}_s t} \; K(\tau)\, e^{i\tau\mathcal{L}_s} \; e^{-it\mathcal{L}_s} \; \bar{\sigma}(t)}$$

$$\frac{d\bar{\sigma}(t)}{dt} = e^{i\mathcal{L}_s t} \underbrace{\left\{ -\int_0^\infty d\tau \; K(\tau)\, e^{i\tau\mathcal{L}_s} \right\}}_{\mathcal{R}} e^{-it\mathcal{L}_s} \; \bar{\sigma}(t)$$

$\mathcal{R}$ – the Redfield relaxation superoperator

In the fairly general situation that the system-bath interaction can be written as a sum of system-bath products,

$$V = \sum_a \underset{\substack{\uparrow \\ \text{bath}}}{F_a} \; \underset{\substack{\uparrow \\ \text{system}}}{G_a}$$

we can further analyze the system relaxation superoperator $K(\tau)$ (and hence $\mathcal{R}$).

We show on pp. (d) and (e)

$$\mathcal{R}\,\hat{O}_s = -\int_0^\infty d\tau \;\; K(\tau)\, e^{i\tau\mathcal{L}_s}\,\hat{O}_s$$

$$= \sum_a \sum_b \int_0^\infty d\tau \;\Big\{ \langle F_a(\tau) F_b \rangle \,[G_b(-\tau)\hat{O}_s ,\, G_a]$$

$$+ \langle F_b F_a(\tau) \rangle \,[G_a ,\, \hat{O}_s G_b(-\tau)] \Big\}$$

where

$$F_a(t) = e^{i\mathcal{L}_b t}\,F_a$$

$$G_b(t) = e^{i\mathcal{L}_s t}\,G_b$$

etc.

N.B. In the special case where $\hat{O}_s$ is a HERMITIAN system operator, the first term in curly brackets is the hermitian conjugate of the second.

we follow Pollard & Friesner [JCP 100, 5054 (1994)]

$$\boxed{\mathcal{R}\,\hat{o}_s = \sum_a \left\{ [G_a^+ \hat{o}_s, G_a] + [G_a, \hat{o}_s G_a^-] \right\}}$$

agrees w/ Eq. (13) of Pollard & Friesner

where

$$G_a^+ = \sum_b \int_0^\infty d\tau \, \langle F_a(\tau) F_b \rangle \, G_b(-\tau) \equiv \sum_b (\Theta_{ab}^+ G_b)$$

$$G_a^- = \sum_b \int_0^\infty d\tau \, \langle F_b F_a(\tau) \rangle \, G_b(-\tau) \equiv \sum_b (\Theta_{ba}^- G_b)$$

parentheses signify that the superoperators Θ_{ab}^+ and Θ_{ba}^- operate on G_b only

$$\Theta_{ab}^+ = \int_0^\infty d\tau \, \langle F_a(\tau) F_b \rangle \, e^{-i\mathcal{L}_s \tau}$$

$$\Theta_{ab}^- = \int_0^\infty d\tau \, \langle F_a F_b(\tau) \rangle \, e^{-i\mathcal{L}_s \tau} = \int_0^\infty d\tau \, \langle F_a(-\tau) F_b \rangle \, e^{-i\mathcal{L}_s \tau}$$

Our basic expression for $\mathcal{R}\hat{o}_s$ agrees with Pollard & Friesner, but has been obtained without specific appeal to the system eigen-energy basis. G_a^+ and G_a^- are ordinary Hilbert-space operators, so evaluation of Pollard & Friesner's expression involves only $N \times N$ matrix multiplication scaling as N^3 (where N is the number of basis vectors), rather than $N^2 \times N^2$-tensor times $N \times N$-matrix multiplication scaling as N^4. *

* See further comments on p. f

In principle, we could start from properties of the bath correlation functions $\langle F_a(\tau) F_b \rangle$ and demonstrate that $\sigma_{eq} = \dfrac{e^{-\beta H_s}}{Z_s}$ is a steady state of the Redfield evolution equation

$$\frac{d\sigma}{dt} = -i\mathcal{L}_s\,\sigma(t) + \mathcal{R}\,\sigma(t) .$$

Instead we proceed by assuming this to be the case, and so set

$$0 = \mathcal{R}\,\sigma_{eq} = \sum_a \sum_b \int_0^\infty d\tau \left\{ \langle F_a(\tau) F_b \rangle \left[G_b(-\tau)\,\sigma_{eq} , G_a \right] + \langle F_b F_a(\tau) \rangle \left[G_a , \sigma_{eq}\, G_b(-\tau) \right] \right\} .$$

We then determine sufficient conditions on the bath correlation functions to ensure this, and ask whether these conditions are in fact obeyed.

$$0 = \sum_a \sum_b \left\{ \left[(\Theta^+_{ab}\, G_b)\,\sigma_{eq} , G_a \right] + \left[G_a , \sigma_{eq}\,(\Theta^-_{ba}\, G_b) \right] \right\}$$

Defining ordinary functions of ω

$$(\Theta^\pm_{ab})_\omega = \int_0^\infty d\tau \,\langle F_a(\pm\tau) F_b \rangle\, e^{-i\omega t} ,$$

taking matrix elements in the eigen energy basis, and using $(\sigma_{eq})_{ij} = \delta_{ij} \dfrac{e^{-\beta \varepsilon_i}}{Z_s} = \delta_{ij}\, p_i$, we find

$$= (O)_{ik} = \sum_a \sum_b \sum_j \Big\{ (\Theta^+_{ab})_{\omega_{ij}} (G_b)_{ij}\, p_j\, (G_a)_{jk}$$

$$- (G_a)_{ij} (\Theta^+_{ab})_{\omega_{jk}} (G_b)_{jk}\, p_k$$

$$+ (G_a)_{ij}\, p_j\, (\Theta^-_{ba})_{\omega_{jk}} (G_b)_{jk}$$

$$- p_i (\Theta^-_{ba})_{\omega_{ij}} (G_b)_{ij} (G_a)_{jk} \Big\}$$

We interchange the roles of a and b in the 2nd & third terms, and get

$$0 = \sum_a \sum_b \sum_j \Big\{ (\Theta^+_{ab})_{\omega_{ij}}\, p_j - (\Theta^+_{ba})_{\omega_{jk}}\, p_k$$

$$+ (\Theta^-_{ab})_{\omega_{jk}}\, p_j - (\Theta^-_{ba})_{\omega_{ij}}\, p_i \Big\} (G_b)_{ij} (G_a)_{jk}$$

A sufficient condition for stationary populations $(i=k)$ and coherences $(i \neq k)$ is that

$$\boxed{(\Theta^+_{ab})_{\omega_{ij}}\, p_j + (\Theta^-_{ab})_{\omega_{jk}}\, p_j = (\Theta^+_{ba})_{\omega_{jk}}\, p_k + (\Theta^-_{ba})_{\omega_{ij}}\, p_i}$$

for all i, j, and k.

OK, agrees w/ previous deriv'n. For the case $k=i$, it also agrees w/ 16 May 94 p. 12.

Conditions on the half-Fourier transforms of the bath correlation functions at system Bohr frequencies ensure equilibration of the system (or at least ensure that the equilibrium state is a steady state).

If we replace ω_{ij} by ω and ω_{kj} by ω' we get

$$(\theta^{+}_{ab})_{\omega} + (\theta^{-}_{ab})_{-\omega'} = (\theta^{+}_{ba})_{-\omega'}e^{-\beta\omega'} + (\theta^{-}_{ba})_{\omega}e^{-\beta\omega}.$$

In this form, the condition for supporting an equilibrium steady state of the system involves NO SPECIFIC INFORMATION ABOUT THE SYSTEM ITSELF; only the bath correlation functions are involved*. As the frequencies ω and ω' are arbitrary and independent, the condition reduces simply to

$$\boxed{(\theta^{+}_{ab})_{\omega} = e^{-\beta\omega}(\theta^{-}_{ba})_{\omega}}$$

sufficient condition for the bath to support an equilibrium state of the system.

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* On pp (g)-(i) it's shown that the **detailed balance condition** (steady-state thermal populations),
$$(\theta^{+}_{ab})_{\omega} + (\theta^{-}_{ab})_{-\omega} = [(\theta^{+}_{ba})_{-\omega} + (\theta^{-}_{ba})_{\omega}]e^{-\beta\omega},$$
is nothing more than the **fluctuation-dissipation theorem** for the bath.

Does our expression for $K(\tau)$ on p. 6 agree with that on p. 4 of $\boxed{\text{16 May 94}}$?

$$Q\mathcal{L}_V \rho_b \hat{O} = \mathcal{L}_V \rho_b \hat{O} - P\mathcal{L}_V \rho_b \hat{O} = \mathcal{L}_V \rho_b \hat{O} - \rho_b \,\mathrm{Tr}_b(\mathcal{L}_V \rho_b)\hat{O}$$

$\hat{O}$ ↑ system operator

$$= \mathcal{L}_V \rho_b \hat{O} - \rho_b \,\mathrm{Tr}_b [V, \rho_b \hat{O}]$$

$$= \mathcal{L}_V \rho_b \hat{O} - \rho_b \,\mathrm{Tr}_b V \rho_b \hat{O} + \rho_b \,\mathrm{Tr}_b \rho_b \hat{O} V$$

$$= \mathcal{L}_V \rho_b \hat{O} - \rho_b \boxed{\sum_{n_b} \langle n_b | V | n_b \rangle p(n_b)} \hat{O} + \rho_b \hat{O} \boxed{\sum_{n_b} p(n_b) \langle n_b | V | n_b \rangle}$$

⟹ both zero $\langle V \rangle = 0$

$$= \mathcal{L}_V \rho_b \hat{O}$$

so the two expressions for $K(\tau)$ are the same.

$\langle V \rangle = 0$ is the reason.

(b)

In the same vein, we can ask whether the Q is needed in the exponent of

$$K(\tau) = \mathrm{Tr}_b \left(\mathcal{L}_v \, e^{-i\tau Q(\mathcal{L}_s + \mathcal{L}_b)} \mathcal{L}_v \rho_b \right)$$

$$e^{-i\tau Q(\mathcal{L}_s+\mathcal{L}_b)} \mathcal{L}_v \rho_b \underbrace{\hat{O}_s}_{\text{system operator}} = \left(e^{-i\frac{\tau}{N} Q(\mathcal{L}_s+\mathcal{L}_b)} \right)^N \mathcal{L}_v \rho_b \hat{O}_s ,$$

where N is large enough so that for each exponential factor $e^{-i\frac{\tau}{N} Q(\mathcal{L}_s+\mathcal{L}_b)} \cong 1 - \frac{i\tau}{N} Q(\mathcal{L}_s+\mathcal{L}_b)$.

First consider the general situation.

$$e^{-i\frac{\tau}{N} Q(\mathcal{L}_s+\mathcal{L}_b)} \underbrace{\hat{a}_b}_{\text{bath}} \underbrace{\hat{a}_s}_{\text{system}} = \hat{a}_b \hat{a}_s - \frac{i\tau}{N} Q(\mathcal{L}_s+\mathcal{L}_b)\, \hat{a}_b \hat{a}_s$$

$$= e^{-i\frac{\tau}{N}(\mathcal{L}_s+\mathcal{L}_b)} \hat{a}_b \hat{a}_s - i\frac{\tau}{N} P(\mathcal{L}_s+\mathcal{L}_b)\, \hat{a}_b \hat{a}_s$$

$$= \hat{a}_b(-\tau/N)\, \hat{a}_s(-\tau/N) - \frac{i\tau}{N} \rho_b \left(\mathrm{Tr}_b\, \hat{a}_b \right) \mathcal{L}_s \hat{a}_s - \frac{i\tau}{N} \rho_b \underbrace{\left(\mathrm{Tr}_b\, \mathcal{L}_b \hat{a}_b \right)}_{0} \hat{a}_s$$

where

$$\hat{a}_b(t) \equiv e^{it\mathcal{L}_b} \hat{a}_b \; ; \quad \hat{a}_s(t) = e^{it\mathcal{L}_s} \hat{a}_s$$

$$\therefore \quad \boxed{e^{-i\frac{\tau}{N}Q(\mathcal{L}_s+\mathcal{L}_b)}\hat{a}_b\hat{a}_s = \hat{a}_b(-\tau/N)\,\hat{a}_s(-\tau/N) - i\frac{\tau}{N}\mathcal{P}\hat{a}_b\mathcal{L}_s\hat{a}_s}$$

In other words, the Q is superfluous if it happens That $\mathcal{P}\hat{a}_b = 0$.

Without loss of generality, we may assume

$$\underset{\substack{\uparrow \\ \text{bath}}}{V = F}\,\underset{\substack{\uparrow \\ \text{system}}}{G}.$$ Then $\langle V\rangle = \mathrm{Tr}_b\,\rho_b V = 0$ requires $\langle F\rangle = 0$

$$e^{-i\frac{\tau}{N}Q(\mathcal{L}_s+\mathcal{L}_b)}\mathcal{L}_V\rho_b\hat{O}_s = e^{-i\frac{\tau}{N}Q(\mathcal{L}_s+\mathcal{L}_b)}[FG, \rho_b\hat{O}_s]$$

$$= e^{-i\frac{\tau}{N}Q(\mathcal{L}_s+\mathcal{L}_b)}(F\rho_b)(G\hat{O}_s) - e^{-i\frac{\tau}{N}Q(\mathcal{L}_s+\mathcal{L}_b)}(\rho_b F)(\hat{O}_s G)$$

each term of which has the prescribed system - bath product form.

Since $\mathcal{P}F\rho_b = \rho_b\mathrm{Tr}_b(F\rho_b) = 0$ and $\mathcal{P}\rho_b F$ vanishes similarly, we have

$$e^{-i\frac{\tau}{N}Q(\mathcal{L}_s+\mathcal{L}_b)}\mathcal{L}_V\rho_b\hat{O}_s = e^{-i\frac{\tau}{N}(\mathcal{L}_s+\mathcal{L}_b)}\{(F\rho_b)(G\hat{O}_s) - (\rho_b F)(\hat{O}_s G)\}$$

$$= F(-\tfrac{\tau}{N})\rho_b\cdot G(-\tfrac{\tau}{N})\hat{O}_s(-\tfrac{\tau}{N}) - \rho_b F(-\tfrac{\tau}{N})\cdot\hat{O}_s(-\tfrac{\tau}{N})G(-\tfrac{\tau}{N})$$

ⓓ

The helpful aspect is that $\mathcal{P}\, F(-\frac{T}{N})\, \rho_b = \mathcal{P}\, \rho_b\, F(-\frac{T}{N}) = 0$, so the same simplification happens when we multiply by the next, and each successive, factor $e^{-i\frac{T}{N} Q(\mathcal{L}_b + \mathcal{L}_s)}$.

Thus

$$\boxed{e^{-i\tau Q(\mathcal{L}_s + \mathcal{L}_b)}\, \mathcal{L}_V\, \rho_b = e^{-i\tau(\mathcal{L}_s + \mathcal{L}_b)}\, \mathcal{L}_V\, \rho_b}$$

in operation on any pure system operator, and we can drop Q from the exponent of $K(T)$ (p. ⑥).

For $V = \sum_a F_a G_a$,

$$K(T)\,\hat{O}_s \underset{\text{p. ⑥}}{\overset{\uparrow}{=}} \sum_a \sum_b \mathrm{Tr}_b \left\{ \left[F_a G_a,\ e^{-i\tau(H_s + H_b)} [F_b G_b, \rho_b \hat{O}_s]\, e^{i\tau(H_s + H_b)} \right] \right\}$$

$$= \sum_a \sum_b \underset{\text{bath, not index } b}{\mathrm{Tr}_b} \left\{ \left[F_a G_a,\ \left[F_b(-\tau) G_b(-\tau),\ \rho_b\, \hat{O}_s(-\tau) \right] \right] \right\}$$

$$F_b(t) = e^{iH_b t}\, F_b\, e^{-iH_b t}$$

$$G_b(t) = e^{iH_s t}\, G_b\, e^{-iH_s t}$$

$$\hat{O}_s(t) = e^{iH_s t}\, \hat{O}_s\, e^{-iH_s t}$$

e

$$K(\tau)\hat{O}_s = \sum_a \sum_b \mathrm{Tr}_b\Big\{ F_a G_a F_b(-\tau) G_b(-\tau) \rho_b \hat{O}_s(-\tau)$$

$$- F_a G_a \rho_b \hat{O}_s(-\tau) F_b(-\tau) G_b(-\tau)$$

$$+ \rho_b \hat{O}_s(-\tau) F_b(-\tau) G_b(-\tau) F_a G_a$$

$$- F_b(-\tau) G_b(-\tau) \rho_b \hat{O}_s(-\tau) F_a G_a \Big\}$$

$$= \sum_a \sum_b \Big\{ \langle F_a F_b(-\tau)\rangle G_a G_b(-\tau) \hat{O}_s(-\tau)$$

$$- \langle F_b(-\tau) F_a\rangle G_a \hat{O}_s(-\tau) G_b(-\tau)$$

$$+ \langle F_b(-\tau) F_a\rangle \hat{O}_s(-\tau) G_b(-\tau) G_a$$

$$- \langle F_a F_b(-\tau)\rangle G_b(-\tau) \hat{O}_s(-\tau) G_a \Big\}$$

$$\boxed{\begin{aligned} (\tau)\hat{O}_s = \sum_a \sum_b \Big\{ &\langle F_a F_b(-\tau)\rangle \left[G_a, G_b(-\tau)\hat{O}_s(-\tau)\right] \\ &+ \langle F_b(-\tau) F_a\rangle \left[\hat{O}_s(-\tau) G_b(-\tau), G_a\right] \Big\} \end{aligned}}$$

OK, repeats

It is worth noting the following about the computational advantage that comes from expressing the operation of $\mathcal{R}$ in terms of ordinary operator multiplication. Pollard & Friesner obtained that expression (in the context of Redfield theory) for the case where the system-bath interaction is a sum of system-bath products. Were this form assumed without making the Markovian assumption of Redfield theory, the system operator in the relaxation term on p. (9), $\hat{O}_s = e^{-i\mathcal{L}_s t}\tilde{\sigma}(t-\tau)$, would have been explicitly τ-dependent. While the τ-integration could no longer be performed "up front" owing to the non-Markovian relaxation, a computational advantage would still be conferred by evaluating the <u>integrand</u> in terms of ordinary operators rather than $N^2 \times N^2$ tensors.

Landau and Lifshitz Statistical Physics, Eq. (125.10)

states the Fluctation-Dissipation theorem as

$$\boxed{(F_a F_b)_\omega = \frac{i}{2}\left(\alpha^*_{ba}(\omega) - \alpha_{ab}(\omega)\right)\coth\frac{\beta\omega}{2}}$$

where the susceptibility is (L & L, Eq. (126.9))

$$\alpha_{ab}(\omega) \equiv i\int_0^\infty dt\, e^{i\omega t} \langle F_a(t) F_b - F_b F_a(t)\rangle .$$

In Pollard's notation the susceptibility would be written

$$\boxed{\alpha_{ab}(\omega) \equiv i(\theta^+_{ab})_{-\omega} - i(\theta^-_{ba})_{-\omega}}.$$

What is meant by the **spectral density**, $(F_a F_b)_\omega$?

L & L's Eq. (125.4) defines it via

$$2\pi (F_a F_b)_\omega\, \delta(\omega+\omega') = \frac{1}{2}\langle F_{a\omega} F_{b\omega'} + F_{b\omega'} F_{a\omega}\rangle$$

$$\equiv \int_{-\infty}^{\infty} dt'\, e^{i\omega t'} \int_{-\infty}^{\infty} dt\, e^{i\omega' t} \langle F_a(t') F_b(t) + F_b(t) F_a(t')\rangle$$

let $t' = t + \tau$

$$= \int_{-\infty}^{\infty} dt\, e^{i(\omega+\omega')t} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \frac{1}{2}\langle F_a(\tau) F_b + F_b F_a(\tau)\rangle$$

$$= 2\pi\delta(\omega+\omega') \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \frac{1}{2}\langle F_a(\tau) F_b + F_b F_a(\tau)\rangle$$

$$
\begin{aligned}
&(\theta^+_{ab})_\omega + \cancel{(\theta^-_{ba})_\omega} + (\theta^-_{ab})_{-\omega} + \cancel{(\theta^+_{ba})_{-\omega}} \\
&\quad + (\theta^+_{ba})^*_\omega - \cancel{(\theta^-_{ab})^*_\omega} + (\theta^+_{ab})_\omega - \cancel{(\theta^-_{ba})_\omega} \\
&= e^{-\beta\omega}\Big\{ \cancel{(\theta^+_{ab})_\omega} + (\theta^-_{ba})_\omega + \cancel{(\theta^-_{ab})_{-\omega}} + (\theta^+_{ba})_{-\omega} \\
&\quad - \cancel{(\theta^+_{ba})^*_\omega} + (\theta^-_{ab})^*_\omega - \cancel{(\theta^+_{ab})_\omega} + (\theta^-_{ba})_\omega \Big\}
\end{aligned}
$$

we've used the "hermition" property

$$(\theta^+_{ab})^*_\omega = (\theta^-_{ba})_{-\omega} .$$

The final expression of the fluctuation-dissipation theorem is then

$$\boxed{(\theta^+_{ab})_\omega + (\theta^-_{ab})_{-\omega} = e^{-\beta\omega}\left[(\theta^-_{ba})_\omega + (\theta^+_{ba})_{-\omega} \right]}$$

whence

$$(F_a F_b)_\omega = \frac{1}{2}\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \langle F_a(\tau) F_b + F_b F_a(\tau)\rangle$$

$$= \frac{1}{2}\int_{0}^{\infty} d\tau\, e^{i\omega\tau} \langle F_a(\tau) F_b + F_b F_a(\tau)\rangle$$

$$+ \frac{1}{2}\int_{0}^{\infty} d\tau'\, e^{-i\omega\tau'} \langle F_a(-\tau') F_b + F_b F_a(-\tau')\rangle$$

$$\boxed{(F_a F_b)_\omega = \frac{1}{2}\left\{ (\Theta^{+}_{ab})_{-\omega} + (\Theta^{-}_{ba})_{-\omega} + (\Theta^{-}_{ab})_{\omega} + (\Theta^{+}_{ba})_{\omega} \right\}}$$

combining the expressions, and changing the sign of ω, we can express the FDT as

$$\frac{1}{2}\left\{ (\Theta^{+}_{ab})_{\omega} + (\Theta^{-}_{ba})_{\omega} + (\Theta^{-}_{ab})_{-\omega} + (\Theta^{+}_{ba})_{-\omega} \right\}$$

$$= -\frac{i}{2}\coth\frac{\beta\omega}{2}\left\{ -i(\Theta^{+}_{ba})^{*}_{\omega} + i(\Theta^{-}_{ab})^{*}_{\omega} - i(\Theta^{+}_{ab})_{\omega} + i(\Theta^{-}_{ba})_{\omega} \right\}$$

$$= \frac{1}{2}\,\frac{1+e^{-\beta\omega}}{1-e^{-\beta\omega}}\left\{ -(\Theta^{+}_{ba})^{*}_{\omega} + (\Theta^{-}_{ab})^{*}_{\omega} - (\Theta^{+}_{ab})_{\omega} + (\Theta^{-}_{ba})_{\omega} \right\}$$