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. in interaction vs. Schrödinger rep - how does this issue connect with our assumption that bath relaxation is rapid compared with system bohr frequencies?
\[ H = H_s + H_b + V \]

Electronic system-bath interaction

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

\[ \mathcal{P} A \equiv \rho_b \text{Tr}_b A \quad \text{where} \quad \rho_b = \frac{e^{-\beta H_b}}{Z_b} \]

\[ Q = 1 - \mathcal{P} \]

\[ \frac{i}{dt} \mathcal{Q} \rho = \mathcal{Q} \mathcal{L} \rho + \mathcal{L} \mathcal{Q} \rho \]

\[ \frac{i}{dt} \mathcal{Q} \rho = \mathcal{Q} \mathcal{L} \rho + \mathcal{L} \mathcal{Q} \rho \Rightarrow \quad \frac{i}{dt} (e^{i \mathcal{Q} \mathcal{L} t} \rho) = e^{it \mathcal{Q} \mathcal{L}} \rho \mathcal{Q} \rho \]

Formal soln:

\[ e^{it \mathcal{Q} \mathcal{L}} \rho(t) = \rho(0) - i \int_0^t e^{i \tau \mathcal{Q} \mathcal{L}} \mathcal{Q} \mathcal{L}^{\dagger} \rho(\tau) \ d\tau \]

\[ \rho(t) = e^{-it \mathcal{Q} \mathcal{L}} \rho(0) - i \int_0^t e^{i \tau \mathcal{Q} \mathcal{L}} \mathcal{Q} \mathcal{L}^{\dagger} \rho(\tau) \ d\tau \]

Substitution gives a closed integro-differential equation for \( \rho(t) \):

\[ \frac{i}{dt} \rho(t) = \mathcal{L} \rho(t) + \mathcal{L} e^{-it \mathcal{Q} \mathcal{L}} \rho(0) - i \int_0^t \mathcal{L} e^{-i(\tau-t) \mathcal{Q} \mathcal{L}} \mathcal{Q} \mathcal{L}^{\dagger} \rho(\tau) \ d\tau \]
\[ \mathcal{D}_b \rho A = \rho_b \text{Tr}_b \left[ (L_b + L^2 + L) \rho_b \text{Tr}_b A \right] \]

\[ = \rho_b \left( \text{Tr}_b \rho_b \right) L_b \text{Tr}_b A + \rho_b \text{Tr}_b \left[ V, \rho_b \text{Tr}_b A \right] \]

\[ = \mathcal{P}_b L_b A + \rho_b [\langle V \rangle, \text{Tr}_b A] \]

\[ \mathcal{P}_b = \mathcal{P}_b L_b \]

if we set things up with

\[ \langle V \rangle \equiv \text{Tr}_b \rho_b V = 0 \]

we can easily do this: if

\[ \langle V_{\text{old}} \rangle \neq 0 \], write

\[ V_{\text{old}} = V_{\text{old}} - \langle V_{\text{old}} \rangle + \langle V_{\text{old}} \rangle \]

call this and incorporate this system operator in \( H_b \).

\[ \mathcal{P}_b \rho L_b A = \rho_b \text{Tr}_b L_b A - \rho_b \text{Tr}_b L_b \rho_b \text{Tr}_b A \]

\[ = \rho_b L_b \text{Tr}_b A - \rho_b \left( \text{Tr}_b \rho_b \right) L_b \text{Tr}_b A = 0 \]

\[ \mathcal{P}_b \rho A = \rho_b \text{Tr}_b \left[ H_b, \rho A \right] = 0 \]

\[ \mathcal{P} \rho Q = \mathcal{P} \rho \text{Tr}_b Q \]
\[
QdPA = 2PA - \bar{QdPA} = 2PA - \bar{L}_x PA
\]
see above, p. 3

\[
= \bar{L}_b PA + \bar{L}_v PA \Rightarrow \Box \quad QdP = \bar{L}_v P
\]

\[
\frac{d}{dt} \bar{P}(t) = \bar{L}_x P(t) + \bar{L}_v e^{-itQdP}
\]

\[
t- \bar{L}_v P(t) = e^{-itQdP}
\]

Can we do anything with the \( \bar{Q}(0) \) term?

\[
\frac{d}{dt} e^{-itQdP} = QdP e^{-itQdP}
\]

\[
\frac{d}{dt} \left( e^{-itQdP} \right) = e^{-itQdP} \left( \bar{L}_x P + \bar{L}_v \right)
\]

\[
e^{-itQdP} = e^{itQdP} \bar{L}_v e^{-itQdP}
\]

\[
e^{-itQdP} = e^{-itQdP} \left( -QdP + \bar{L}_x P \right)
\]

\[
e^{-itQdP} = e^{-itQdP} \bar{L}_v e^{-itQdP}
\]

\[
e^{-itQdP} = e^{-itQdP} \left( -QdP + \bar{L}_x P \right)
\]

\[
\frac{d}{dt} e^{-itQdP} = e^{-itQdP} \left( \bar{L}_x P + \bar{L}_v \right)
\]

\[
e^{-itQdP} = e^{-itQdP} \left( -QdP + \bar{L}_x P \right)
\]

\[
e^{-itQdP} = e^{-itQdP} \bar{L}_v e^{-itQdP}
\]
\[
\frac{d}{dt} \rho(t) = L_S \rho(t) + P_L e^{-i(t-t')Q(S+S_b)} Q \rho(0) \\
\int_0^t dt' P_L e^{-i(t-t')Q(S+S_b)} Q L e^{-i(t-t')Q(S+S_b)} Q \rho(0) \\
\int_0^t dt' L e^{-i(t-t')Q(S+S_b)} L \rho(t') 
\]

We assume (and will check later) that \( t \) 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 \( e^{-i(t-t')Q(S+S_b)} \approx e^{-i(t-t')Q(S+S_b)} \) in the first integrand and \( e^{-i(t-t')Q(S+S_b)} \approx e^{-i(t-t')Q(S+S_b)} \) in the second.

* This assumption is unjustified so far: We've specified the form of \( \rho_b \), but not of \( S \) nor \( \rho(0) \)!
Things get markedly simpler looking if we specialize to
the situation \( Q\rho(0) = 0 \):

\[
\frac{d\rho(t)}{dt} = L_s \rho(t) - i \int_0^t d\tau \ \mathcal{L}_\nu e^{-(t-\tau)Q(L_s + L_b)} L_\nu \rho(t)
\]

we define the REDUCED DENSITY MATRIX of the system as

\( \sigma(t) \equiv Tr_b \rho(t) \). Then \( \dot{\rho}(t) = \rho_b \sigma(t) \), and

\[
\frac{i d\sigma(t)}{dt} = L_s \sigma(t) - i \int_0^t d\tau \ \mathcal{L}_\nu \sigma(t) e^{-(t-\tau)Q(L_s + L_b)} L_\nu \rho_b \sigma(t)
\]

\[
= L_s \sigma(t) - i \int_0^t d\tau \ K(\tau) \sigma(t-\tau)
\]

\( \tau' = t - \tau \Rightarrow \tau = -\tau' \) \( d\tau = -d\tau' \)

where \( K(\tau) = Tr_b(L_\nu e^{-i\tau Q(L_s + L_b)} L_\nu \rho_b) \)

is the RELAXATION SUPEROPERATOR.

On pp. (b-d) it's shown that the \( Q \) in the exponent is superfluous:

\[
K(\tau) = Tr_b(L_\nu e^{-i\tau(L_s + L_b)} L_\nu \rho_b)
\]
In the interaction picture $\bar{\sigma}(t) = e^{i\Delta t}\sigma(t)$

\[
\frac{d}{dt}\bar{\sigma}(t) = -i \int_0^t d\tau e^{i\Delta t} K(\tau) \bar{\sigma}(t-\tau)
\]

\[
= -i \int_0^t d\tau e^{i\Delta t} K(\tau) e^{-i\Delta s(t-\tau)} \bar{\sigma}(t-\tau)
\]

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

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

\[
\frac{d}{dt}\bar{\sigma}(t) = -i \int_0^t d\tau e^{i\Delta t} K(\tau) \bar{\sigma}(t-\tau) = -i\Delta s \bar{\sigma}(t)
\]

Once $t$ exceeds the "bath relaxation time" $\tau_r$ (decay time of $K(t)e^{i\Delta t}$), the upper integration limit can be replaced by $\infty$. 

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

\[ \Delta \sigma_{\text{slippage}} \sim -T_{\text{rel}} \int_0^\infty dt \; K(t) \; e^{iL_s^z t} \sigma(0) , \]

in the reduced density matrix (Schrödinger picture).

By the weak coupling assumption, this is a small mistake, so we finally arrive at

\[ \frac{d \sigma(t)}{dt} = -\int_0^\infty dt \; e^{iL_s^z t} \; K(t) \; e^{iL_s^z t} \sigma(t) \]

\[ \frac{d \sigma(t)}{dt} = e^{iL_s^z t} \left\{ -\int_0^\infty dt \; K(t) \; e^{iL_s^z t} \right\} e^{-iL_s^z t} \sigma(t) \]

\[ \mathcal{R} \quad \text{the Redfield relaxation superoperator} \]
In the fairly general situation that the system-bath interaction can be written as a sum of system-bath products,

\[ Y = \sum_{\alpha \uparrow \downarrow} \alpha_{\text{bath}} \alpha_{\text{system}} \]

we can further analyze the superoperator \( \hat{K}(\tau) \) (and hence \( \hat{R} \)).

We show on pp. \( \circ \) and \( \circ \)

\[ \hat{R} \hat{\delta}_{s} = -\int_{0}^{\infty} \hat{K}(\tau) e^{i\tau \hat{\delta}_{s}} \hat{\delta}_{s} \]

\[ = \sum_{\alpha \beta} \int_{0}^{\infty} \{ \langle F_{\alpha}(\tau) F_{\beta} \rangle \ [G_{\beta}(\tau) \hat{\delta}_{s}, G_{\alpha}] \\
+ \langle F_{\beta} F_{\alpha}(\tau) \rangle \ [G_{\alpha}, \hat{\delta}_{s} G_{\beta}(\tau)] \} \]

where

\[ F_{\alpha}(t) = e^{-iE_{\alpha}t} F_{\alpha} \]

\[ G_{\beta}(t) = e^{-iE_{\beta}t} G_{\beta} \]

etc.

N.B. In the special case where \( \hat{\delta}_{s} \) 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)]

\[ R \hat{\alpha} = \sum \{ [G^+_a, \hat{\alpha}_a, G_a] + [G_a, \hat{\alpha}_a, G^-_a] \} \]

where

\[ G^+_a = \sum_b \int_0^\infty \langle F_a(t) F_b \rangle \ G_b(-\tau) e^{\sum_b (\theta^+_{ab} \ G_b)} \]

\[ G^-_a = \sum_b \int_0^\infty \langle F_b F_a(t) \rangle \ G_b(-\tau) e^{\sum_b (\theta^-_{ba} \ G_b)} \]

\[ \theta^+_{ab} = \int_0^\infty \langle F_a(t) F_b \rangle e^{-i \omega \tau} \]

\[ \theta^-_{ab} = \int_0^\infty \langle F_a F_b(t) \rangle e^{-i \omega \tau} = \int_0^\infty \langle F_a(-\tau) F_b \rangle e^{-i \omega \tau} \]

Our basic expression for \( R \hat{\alpha} \) 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 involved 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. 5*
In principle, we could start from properties of the bath correlation functions \( \langle F_a(t) F_b \rangle \) and demonstrate that \( \sigma_{eq} = \frac{e^{-\beta H_0}}{Z_s} \) is a steady state of the Redfield evolution equation.

\[
\frac{d\sigma}{dt} = -i\mathcal{L}_\sigma \sigma(t) + \mathcal{R} \sigma(t).
\]

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

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

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 \( \omega \)

\[
(\Theta_{ab})_\omega = \int_0^\infty dt \langle F_a(\pm t) F_b \rangle e^{-i\omega t},
\]

taking matrix elements in the eigen energy basis, and using \( (\sigma_{eq})_{ij} = \delta_{ij} \frac{e^{-\beta E_i}}{Z_s} = \delta_{ij} \rho_i \), we find
\[ (0)_{ijk} = \sum_{a} \sum_{b} \sum_{j} \{(\theta_{ab}^{+})_{ij} (G_{a})_{ij} \cdot p_{j} (G_{b})_{jk} \}
- (G_{a})_{ij} \cdot (\theta_{ab}^{+})_{ij} (G_{b})_{jk} \cdot p_{k}
+ (G_{a})_{ij} \cdot p_{j} \cdot (\theta_{ba}^{-})_{ij} (G_{b})_{jk}
- p_{i} \cdot (\theta_{ba}^{-})_{ij} (G_{b})_{ij} \cdot (G_{a})_{jk} \}
\]

We interchange the roles of \( a \) and \( b \) in the 2nd 3rd terms, and get

\[ 0 = \sum_{a} \sum_{b} \sum_{j} \{(\theta_{ab}^{+})_{ij} \cdot p_{j} - (\theta_{ba}^{-})_{ij} \cdot w_{jk} \cdot p_{k}
+ (\theta_{ab}^{-})_{ij} \cdot p_{j} - (\theta_{ba}^{-})_{ij} \cdot p_{i} \cdot (G_{b})_{ij} \cdot (G_{a})_{jk} \}
\]

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

\[ (\theta_{ab}^{+})_{ij} \cdot p_{j} + (\theta_{ab}^{-})_{ij} \cdot w_{jk} \cdot p_{j} = (\theta_{ba}^{-})_{ij} \cdot w_{jk} \cdot p_{k} + (\theta_{ba}^{-})_{ij} \cdot w_{ij} \cdot p_{i} \]

for all \( i, j, \) and \( k \).

\[ \text{Or, agrees w/ previous derivn. For the case } k = i, \text{ it also agrees w/ 16 May 94.} \]

v.p. (12).
Conditions on the half-Fourier transforms of the bath correlation functions at system Bohr frequencies ensure equilibrium of the system (or at least ensure that the equilibrium state is a steady state).

If we replace \( w \) by \( w' \) and \( w' \) by \( w \), we get

\[
(\Theta_{ab})_w + (\Theta_{ba})_{-w} = (\Theta_{ba})_{-w} e^{-\beta w'} + (\Theta_{ba})_{w} e^{\beta w}.
\]

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 \( w \) and \( w' \) are arbitrary and independent, the condition reduces simply to

\[
(\Theta_{ab})_w = e^{-\beta w} (\Theta_{ba})_w
\]

\[\text{sufficient condition for the bath to support an equilibrium state of the system.}\]

* On pp.9-11 it's shown that the detailed balance condition (steady-state thermal populations),

\[
(\Theta_{ab})_w + (\Theta_{ba})_{-w} = [(\Theta_{ba})_{-w} + (\Theta_{ba})_w] e^{-\beta w},
\]

is nothing more than the fluctuation-dissipation theorem for the bath.
Does our expression for $K(t)$ on p. 6 agree with that on p. 4 of 16 May 94?

\[ \mathcal{L}_V \rho_b \hat{\delta} = \mathcal{L}_V \rho_b \hat{\delta} - \partial_t \mathcal{L}_V \rho_b \hat{\delta} = \mathcal{L}_V \rho_b \hat{\delta} - \rho_b \text{Tr}_b (\mathcal{L}_V \rho_b) \hat{\delta} \]

system operator

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

= $\mathcal{L}_V \rho_b \hat{\delta} - \rho_b \text{Tr}_b V \rho_b \hat{\delta} + \rho_b \text{Tr}_b \rho_b \hat{\delta} V$

= $\mathcal{L}_V \rho_b \hat{\delta} - \rho_b \sum_{n_b} <n_b | V | n_b> \rho(n_b) \hat{\delta}$

+ $\rho_b \hat{\delta} \sum_{n_b} \rho(n_b) <n_b | V | n_b>$

both zero, $\langle V \rangle = 0$

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

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

$\langle V \rangle = 0$ is the reason.
In the same vein, we can ask whether the $Q_A$ in the exponent of

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

$$e^{-i \tau Q(\mathcal{L}_s + \mathcal{L}_b)} \mathcal{L}_v \rho_b \mathcal{L}_v^{-1} = \left( e^{-i \tau Q(\mathcal{L}_s + \mathcal{L}_b)} \mathcal{L}_v \rho_b \mathcal{L}_v^{-1} \right)^N,$$

where $N$ is large enough so that for each exponential factor

$$e^{-i \tau Q(\mathcal{L}_s + \mathcal{L}_b)} \mathcal{L}_v \rho_b \mathcal{L}_v^{-1} \approx 1 - i \frac{\tau}{N} Q(\mathcal{L}_s + \mathcal{L}_b).$$

First consider the general situation.

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

$$\uparrow \downarrow \text{both system}$$

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

$$= \hat{a}_b (-i \frac{\tau}{N}) \hat{a}_s (-i \frac{\tau}{N}) - i \frac{\tau}{N} \rho_b (Tr_b \hat{a}_b) \mathcal{L}_s \hat{a}_s$$

$$- i \frac{\tau}{N} \rho_b (Tr_b \mathcal{L}_b \hat{a}_b) \hat{a}_s$$

where

$$\hat{a}_b(t) = e^{it \mathcal{L}_b} \hat{a}_b \quad \hat{a}_s(t) = e^{it \mathcal{L}_s} \hat{a}_s.$$
\[ e^{-iQ(\hat{L}_S+\hat{J}_b)/N} \hat{a}_b \hat{a}_S = \hat{a}_b(-\tau/N) \hat{a}_S(-\tau/N) - i\frac{i}{N} \mathcal{P}\hat{a}_b \hat{L}_S \hat{a}_S \]

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

Without loss of generality, we may assume \( V = FG \). Then \( \langle V \rangle = \text{Tr}_b \rho_b V = 0 \) requires \( \langle F \rangle = 0 \) for the bath system

\[ e^{-i\frac{i}{N} Q(\hat{L}_S+\hat{J}_b)} \mathcal{L}_V \rho_b \hat{a}_S = e^{-i\frac{i}{N} Q(\hat{L}_S+\hat{J}_b)} [FG, \rho_b \hat{a}_S] \]

\[ = e^{-i\frac{i}{N} Q(\hat{L}_S+\hat{J}_b)} (F\rho_b)(G\hat{a}_S) - e^{-i\frac{i}{N} Q(\hat{L}_S+\hat{J}_b)} (\rho_b F)(\hat{a}_S G) \]

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

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

\[ e^{-i\frac{i}{N} Q(\hat{L}_S+\hat{J}_b)} \mathcal{L}_V \rho_b \hat{a}_S = e^{-i\frac{i}{N} (\hat{L}_S+\hat{J}_b)} \left\{ (F\rho_b)(G\hat{a}_S) - (\rho_b F)(\hat{a}_S G) \right\} \]

\[ = F(-\frac{i}{N}) \rho_b \cdot G(-\frac{i}{N}) \hat{a}_S(-\frac{i}{N}) - \rho_b F(-\frac{i}{N}) \cdot \hat{a}_S(-\frac{i}{N}) G(-\frac{i}{N}) \]
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 $e^{-i\frac{T}{N} Q (\hat{\sigma}_b + \hat{z}_b)}$.

Thus

\[
e^{-i\frac{T}{N} Q (\hat{\sigma}_b + \hat{z}_b)} \rho_b = e^{-i\frac{T}{N} (\hat{\sigma}_b + \hat{z}_b)} \rho_b
\]

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

For $V = \sum_a F_a G_a$,

\[
K(\tau) \hat{\sigma}_b = \sum_a \sum_b \text{Tr}_b \left\{ \left[ F_a G_a, e^{-i\tau (H_b + H_{\hat{\sigma}})} \right] \left[ F_b G_b, \rho_b \hat{\sigma}_b \right] e^{i\tau (H_b + H_{\hat{\sigma}})} \right\}
\]

\[
= \sum_a \sum_b \text{Tr}_b \left\{ \left[ F_a G_a, \left[ F_b (-\tau) G_b (-\tau), \rho_b \hat{\sigma}_b (-\tau) \right] \right] \left[ F_b G_b, \rho_b \hat{\sigma}_b (-\tau) \right] e^{i\tau (H_b + H_{\hat{\sigma}})} \right\}
\]

\[
F_b (t) = e^{iH_b t} e^{-iH_b t}
\]

\[
G_b (t) = e^{iH_b t} G_b e^{-iH_b t}
\]

\[
\hat{\sigma}_b (t) = e^{iH_{\hat{\sigma}} t} \hat{\sigma}_b e^{-iH_{\hat{\sigma}} t}
\]

\[
\hat{\sigma}_b (t) = e^{iH_{\hat{\sigma}} t} \hat{\sigma}_b e^{-iH_{\hat{\sigma}} t}
\]
\[ K(t) \hat{\Theta}_s = \sum_a \sum_b \text{Tr}_b \left\{ F_a G_a F_b(-t) G_b(-t) \rho_b \hat{\Theta}_s(-t) \right\} \\
- F_a G_a \rho_b \hat{\Theta}_s(-t) F_b(-t) G_b(-t) \\
+ \rho_b \hat{\Theta}_s(-t) F_b(-t) G_b(-t) F_a G_a \\
- F_b(-t) G_b(-t) \rho_b \hat{\Theta}_s(-t) F_a G_a \right\}^{(2)} \\
= \sum_a \sum_b \left\{ \langle F_a F_b(-t) \rangle G_a G_b(-t) \hat{\Theta}_s(-t) \\
- \langle F_b(-t) F_a \rangle G_a \hat{\Theta}_s(-t) G_b(-t) \\
+ \langle F_b(-t) F_a \rangle \hat{\Theta}_s(-t) G_b(-t) G_a \\
- \langle F_a F_b(-t) \rangle G_b(-t) \hat{\Theta}_s(-t) G_a \right\}^{(2)} \\
\]

\[ (t) \hat{\Theta}_s = \sum_a \sum_b \left\{ \langle F_a F_b(-t) \rangle [G_a, G_b(-t) \hat{\Theta}_s(-t)] \\
+ \langle F_b(-t) F_a \rangle [\hat{\Theta}_s(-t) G_b(-t), G_a] \right\}^{(2)} \\
\]

\[ \text{OK, repeats} \]
It is worth noting the following about the computational advantage that comes from expressing the operation of $R$ in terms of ordinary operator multiplication. \( \text{in the context of Redfield theory} \)

Pollard & Friesner obtained that expression 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, \( \hat{\Omega}_S = e^{-i\sigma t} \hat{\sigma}(t-t) \), would have been explicitly $t$-dependent. While the $t$-integration could no longer be performed "up front" owing to the non-Markovian relaxation, a computational advantage would still be conferred by evaluating the integrand in terms of ordinary operators rather than $N^2 \times N^2$ tensors.
Landau and Lifshitz Statistical Physics, Eq. (125.10) states the Fluctuation-Dissipation theorem as

\[
(F_a F_b)_\omega = \frac{i}{2} \left( \chi_{ab}^* (\omega) - \chi_{ab} (\omega) \right) \coth \frac{\beta \omega}{2}
\]

where the susceptibility is \( L \) in \( \omega \), Eq. (126.9)

\[
\chi_{ab} (\omega) \equiv i \int_0^\infty dt e^{i \omega t} \langle F_a (t) F_b - F_b F_a (t) \rangle.
\]

In Pollard's notation, the susceptibility would be written

\[
\chi_{ab} (\omega) \equiv i (\Theta_{ab}^+) - \omega - i (\Theta_{ba}^-) - \omega.
\]

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

L's Eq. (125.4) defines it via

\[
2 \pi (F_a F_b)_\omega \delta (\omega + \omega') = \frac{1}{i} \langle F_a \omega F_b \omega' + F_b \omega F_a \omega \rangle
\]

\[
= \int_{-\infty}^{\infty} dt e^{i \omega t} \int_{-\infty}^{\infty} dt' e^{i \omega t'} \langle F_a (t) F_b (t) + F_b (t) F_a (t') \rangle
\]

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

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

\[
= 2 \pi \delta (\omega + \omega') \int_{-\infty}^{\infty} d\tau e^{i \omega \tau} \frac{1}{2} \langle F_a (\tau) F_b + F_b F_a (\tau) \rangle
\]
\[
(\theta_{ab})_w + (\theta_{ba})_w = e^{-\beta w} \left[ (\theta_{ba})_w + (\theta_{ba})_-w \right]
\]

we've used the "hermitian" property:

\[
(\theta_{ab})^* = (\theta_{ba})_-w
\]

The final expression of the fluctuation-dissipation theorem is then
whence

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

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

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

\[ (F_a F_b)_\omega = \frac{1}{2} \left\{ (\Theta_{a b})_{-\omega} + (\Theta_{b a})_{-\omega} \right. \]

\[ + (\Theta_{a b})_{\omega} + (\Theta_{b a})_{\omega} \]

Combining the expressions, and changing the sign of \( \omega \),

we can express the FDT as

\[ \frac{1}{2} \left\{ (\Theta_{a b})_{\omega} + (\Theta_{b a})_{\omega} + (\Theta_{a b})_{-\omega} + (\Theta_{b a})_{-\omega} \right\} \]

\[ = -i \coth \frac{\beta \omega}{2} \left\{ -i (\Theta_{b a})_{\omega}^* + i (\Theta_{a b})_{\omega}^* \right. \]

\[ -i (\Theta_{a b})_{\omega} + i' (\Theta_{b a})_{\omega} \}

\[ = \frac{1}{2} \left\{ \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \omega}} \right\} \left\{ - (\Theta_{b a})_{\omega}^* + (\Theta_{a b})_{\omega}^* - (\Theta_{a b})_{\omega} + (\Theta_{b a})_{\omega} \right\} \]