Non-Markovian theories based on a decomposition of the spectral density

Ulrich Kleinekathöfer
Dept. of Physics
Chemnitz University of Technology
kleinekathoefer@physik.tu-chemnitz.de
Overview

➤ Introduction

➤ Spectral density and bath correlation function

➤ Nakajima-Zwanzig identity

➤ Hashitsume-Shibata-Takahashi identity

➤ Time-local theory

➤ Time-nonlocal theory

➤ Comparison for damped harmonic oscillator
Time-dependent quantum mechanics

➤ time-dependent Schrödinger equation

\[ i\hbar \frac{d}{dt} |\Psi(x, t)\rangle = H(x, t) |\Psi(x, t)\rangle \]

➤ for time-independent \( H(x) \) the Ansatz \( |\Psi(x, t)\rangle = |\Psi(x)\rangle e^{-iEt/\hbar} \) leads to time-independent Schrödinger equation

\[ H(x) |\Psi(x)\rangle = E |\Psi(x)\rangle \]

➤ time-dependent equation can only be solved for a few degrees of freedom

- 3-5 dimensions with "standard" methods
- up to 15 dimensions with sophisticated methods and small basis per degree of freedom
Density matrices

➤ pure state: $\sigma = |\Psi\rangle\langle\Psi|$

➤ mixed state: $\sigma = \sum_n W_n |\Psi_n\rangle\langle\Psi_n|$

➤ evolution

$$i\hbar \frac{d\sigma(t)}{dt} = i\hbar \frac{d|\Psi\rangle\langle\Psi|}{dt} = i\hbar \left( \frac{d|\Psi\rangle}{dt}\langle\Psi| + |\Psi\rangle \frac{d\langle\Psi|}{dt} \right)$$

$$= [H(t), \sigma(t)]$$

➤ observables:

$$\langle Q \rangle = \langle \Psi | Q | \Psi \rangle = \sum_n \langle \Psi | n \rangle \langle n | Q | \Psi \rangle$$

$$= \sum_n \langle n | Q | \Psi \rangle \langle \Psi | n \rangle = tr(Q\sigma)$$

➤ some global phase information lost
Reduced density matrix formalism

- goal: description of fast (fs) processes in the condensed phase
- full quantum dynamics including temperature dependence, dephasing, energy dissipation, but also coherences
- splitting into relevant system modes and thermal bath

- reduced density matrix approach:
  $\sigma$ - density matrix of the full system (relevant system + bath)
  $\rho = tr_B(\sigma)$ - density matrix of the relevant system

$$i\hbar \frac{d\rho(t)}{dt} = [H_S(t) + H_{\text{laser}}(t), \rho(t)]$$
Reduced density matrix formalism

➤ goal: description of fast (fs) processes in the condensed phase

➤ full quantum dynamics including temperature dependence, dephasing, energy dissipation, but also coherences

➤ splitting into relevant system modes and thermal bath

➤ reduced density matrix approach:

\[ \sigma - \text{density matrix of the full system (relevant system + bath)} \]

\[ \rho = tr_B(\sigma) - \text{density matrix of the relevant system} \]

\[ i\hbar \frac{d\rho(t)}{dt} = [H_S(t) + H_{\text{laser}}(t), \rho(t)] + \mathcal{D}(t)\rho(t) \]
Hamiltonian

➤ system-plus-bath Hamiltonian

\[ H = H_s + H_b + H_{sb} + H_{ren} .\]

➤ time-independent potential \( V(q) \) and laser field \( W(q,t) \)

\[ H_s = \frac{p^2}{2M} + V(q) + W(q,t) .\]

➤ bath Hamiltonian: sum of harmonic oscillators

\[ H_b = \frac{1}{2} \sum_{i=1}^{N} \left( \frac{p_i^2}{m_i} + m_i \omega_i^2 x_i^2 \right) .\]

➤ system-bath interaction: \( H_{sb} = -K(q) \sum_{i=1}^{N} c_i x_i \)
Hamiltonian

➤ renormalization Hamiltonian $H_{ren}$ to avoid artificial shifts in the system potential

$$H_{ren} = K(q)^2 \sum_{i=1}^{N} \frac{c_i^2}{2m_i\omega_i^2} = K(q)^2 \frac{\mu}{2}.$$  

➤ in absence of renormalization:

- minimum of the potential surface for given $q$ at $x_i = \frac{c_iK(q)}{m_i\omega_i^2}$
- for $K(q) = q$ leads to shift $\Delta\omega^2 = -\sum_i c_i^2/(Mm_i\omega_i^2)$
- renormalization term compensates for this shift

➤ bilinear coupling: $F(q) = q \rightarrow$ Caldeira-Leggett Hamiltonian

$$H = \frac{p^2}{2M} + V(t) + W(q, t) + \frac{1}{2} \sum_{i=1}^{N} \left[ \frac{p_i^2}{m_i} + m_i\omega_i^2 \left( x_i - \frac{c_i}{m_i\omega_i^2}q \right)^2 \right].$$
Decomposition of the spectral density

➤ information on the frequencies of the bath modes and their coupling to the system

\[ J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i) \]

➤ property \( J(-\omega) = -J(\omega) \)

➤ numerical decomposition in Lorentzians (Meier and Tannor)

\[ J(\omega) = \sum_{k=1}^{n} \frac{p_k}{4 \Omega_k} \left\{ \frac{1}{(\omega - \Omega_k)^2 + \Gamma_k^2} - \frac{1}{(\omega + \Omega_k)^2 + \Gamma_k^2} \right\} \]

\[ = \sum_{k=1}^{n} p_k \frac{\omega}{[(\omega + \Omega_k)^2 + \Gamma_k^2][\omega - \Omega_k]^2 + \Gamma_k^2]} \]
Decomposition of the spectral density

- Plot of $J(\omega)$
- Fit with 20 Lorentians
Correlation function

➤ using the theorem of residues

\[ C(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} J(\omega) \frac{e^{i\omega t}}{e^{\beta \omega} - 1} = \frac{2i}{\beta} \sum_{k=1}^{n'} J(i\nu_k) e^{-\nu_k t} \]

\[ + \sum_{k=1}^{n} \frac{p_k}{4\Omega_k \Gamma_k} \left\{ e^{i\Omega_k^+ t} n_B(\Omega_k^+) + e^{-i\Omega_k^- t} (n_B(\Omega_k^-) + 1) \right\} \]

➤ with \( \Omega_k^+ = \Omega_k + i\Gamma_k \), \( \Omega_k^- = \Omega_k - i\Gamma_k \), the Bose-Einstein distribution \( n_B(\omega) \) and the Matsubara frequencies \( \nu_k = 2\pi k / \beta \)

➤ in principle, the sum over the Matsubara terms is an infinite one but in practice the sum can be truncated (temperature-dependent)

➤ time dependence in \( C(t) \) is now fully exponential which enables further analytic treatment
Correlation function

- real and imaginary part defined as

\[ C(t) = a(t) - ib(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} J(\omega) \cos(\omega t) \coth\left(\frac{\beta \omega}{2}\right) - i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} J(\omega) \sin(\omega t) \]

with

\[ a(t) = \sum_{k=1}^{n} \frac{p_k}{8\Omega_k \Gamma_k} \left\{ \coth\left(\beta \Omega_k^- / 2\right)e^{-i\Omega_k^- t} + \coth\left(\beta \Omega_k^+ / 2\right)e^{i\Omega_k^+ t} \right\} + \frac{2i}{\beta} \sum_{k=1}^{n'} J(i\nu_k) e^{-\nu_k t} \]

and

\[ b(t) = \sum_{k=1}^{n} \frac{ip_k}{8\Omega_k \Gamma_k} \left\{ e^{-i\Omega_k^- t} - e^{i\Omega_k^+ t} \right\}. \]

Abbreviations

- \( a(t) = \sum_{k=1}^{n_r} \alpha_k^r e^{\gamma_k^r t} \) with \( n_r = 2n + n' \)
- \( b(t) = \sum_{k=1}^{n_i} \alpha_k^i e^{\gamma_k^i t} \) with \( n_i = 2n \)
Correlation function: Drude form

Drude form

\[ J(\omega) = \eta \omega / (1 + (\omega / \omega_d)^2) \]

poles at \( \omega = \pm i \omega_d \)

using theorem of residues yields

\[
a(t) = \frac{\eta}{2} \omega_d^2 \cot(\beta \omega_d / 2)e^{-\omega_d t} - \frac{2\eta}{\beta} \sum_{k=1}^{n'} \frac{\nu_k e^{-\nu_k t}}{1 - (\nu_k / \omega_d)^2}
\]

and

\[
b(t) = \frac{\eta}{2} \omega_d^2 e^{-\omega_d t}.
\]

singularities in \( a(t) \) or \( b(t) \) such as the singularities at \( \nu_k = \omega_d \)

abbreviations

- \( a(t) = \sum_{k=1}^{n_r} \alpha_k^r e^{\gamma_k^r t} \) with \( n_r = n' + 1 \)
- \( b(t) = \alpha_1^i e^{\gamma_1^i t} \) with \( n_i = 1 \)
Nakajima-Zwanzig identity

- Liouville equation $i \frac{d}{dt} \sigma(t) = \mathcal{L} \sigma(t)$ with $\mathcal{L} \ldots = \frac{i}{\hbar}[H, \ldots]$

- For simplicity here $H$ time-independent

- Use projector $P$ onto relevant part of the whole system, $P + Q = 1$, $P = P^2$

- Project onto relevant and irrelevant part

\[
\begin{align*}
  i \frac{d}{dt} P \sigma(t) &= P \mathcal{L} \sigma(t) = P \mathcal{L} P \sigma(t) + P \mathcal{L} (1 - P) \sigma(t) \\
  i \frac{d}{dt} (1 - P) \sigma(t) &= (1 - P) \mathcal{L} \sigma(t) = (1 - P) \mathcal{L} P \sigma(t) + (1 - P) \mathcal{L} (1 - P) \sigma(t)
\end{align*}
\]
Nakajima-Zwanzig identity

➤ Liouville equation $i \frac{d}{dt} \sigma(t) = L \sigma(t)$ with $L \ldots = \frac{1}{\hbar}[H, \ldots]$ 

➤ for simplicity here $H$ time-independent 

➤ use projector $P$ onto relevant part of the whole system, $\mathcal{P} + \mathcal{Q} = 1$, $\mathcal{P} = \mathcal{P}^2$

➤ project onto relevant and irrelevant part

\[
\begin{align*}
  i \frac{d}{dt} \mathcal{P} \sigma(t) &= \mathcal{P} L \sigma(t) = \mathcal{P} L \mathcal{P} \sigma(t) + \mathcal{P} L (1 - \mathcal{P}) \sigma(t) \\
  i \frac{d}{dt} (1 - \mathcal{P}) \sigma(t) &= (1 - \mathcal{P}) L \sigma(t) = (1 - \mathcal{P}) L \mathcal{P} \sigma(t) + (1 - \mathcal{P}) L (1 - \mathcal{P}) \sigma(t)
\end{align*}
\]

➤ solve equation for the irrelevant part

\[
(1 - \mathcal{P}) \sigma(t) = e^{-i(1-\mathcal{P})L(t)} (1 - \mathcal{P}) \sigma(t_0) - i \int_0^t e^{-i(1-\mathcal{P})L(t-\tau)} (1 - \mathcal{P}) L \mathcal{P} \sigma(\tau) d\tau
\]
Nakajima-Zwanzig identity

- Liouville equation \( i \frac{d}{dt} \sigma(t) = \mathcal{L} \sigma(t) \) with \( \mathcal{L} \ldots = \frac{1}{\hbar}[H, \ldots] \)

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\[
\begin{align*}
  i \frac{d}{dt} P \sigma(t) &= \mathcal{P} \mathcal{L} \sigma(t) = \mathcal{P} \mathcal{L} P \sigma(t) + \mathcal{P} \mathcal{L} (1 - P) \sigma(t) \\
  i \frac{d}{dt} (1 - P) \sigma(t) &= (1 - P) \mathcal{L} \sigma(t) = (1 - P) \mathcal{L} P \sigma(t) + (1 - P) \mathcal{L} (1 - P) \sigma(t)
\end{align*}
\]

- solve equation for the irrelevant part

\[
(1 - P) \sigma(t) = e^{-i(1-P)\mathcal{L}(t)} (1 - P) \sigma(t_0) - i \int_0^t e^{-i(1-P)\mathcal{L}(t-\tau)} (1 - P) \mathcal{L} P \sigma(\tau) d\tau
\]

- plug into equation for relevant part to get the Nakajima-Zwanzig identity

\[
\begin{align*}
  \frac{d}{dt} P \sigma(t) &= -i \mathcal{P} \mathcal{L} P \sigma(t) - \int_0^t \mathcal{P} \mathcal{L} e^{-i(1-P)\mathcal{L}(t-\tau)} (1 - P) \mathcal{L} P \sigma(\tau) d\tau \\
  &\quad - i \mathcal{P} \mathcal{L} e^{-i(1-P)\mathcal{L}(t-t_0)} (1 - P) \sigma(t_0)
\end{align*}
\]
Hashitsume-Shibata-Takahashi identity

➤ equation for irrelevant part

\[(1 - \mathcal{P})\sigma(t) = e^{-i(1 - \mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0)\]

\[-i \int_0^t e^{-i(1 - \mathcal{P})\mathcal{L}(t-\tau)}(1 - \mathcal{P})\mathcal{L} \mathcal{P} e^{i\mathcal{L}(t-\tau)}\sigma(t) \, d\tau\]
Hashitsume-Shibata-Takahashi identity

➤ equation for irrelevant part

\[(1 - \mathcal{P})\sigma(t) = e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0)
\]

\[-i \int_0^t e^{-i(1-\mathcal{P})\mathcal{L}(t-\tau)}(1 - \mathcal{P})\mathcal{L} \mathcal{P} e^{i\mathcal{L}(t-\tau)} \sigma(t) d\tau\]

➤ define operator

\[D(t) = i \int_0^t e^{-i(1-\mathcal{P})\mathcal{L}(t-\tau)}(1 - \mathcal{P})\mathcal{L} \mathcal{P} e^{i\mathcal{L}(t-\tau)} d\tau\]

\[(1 - \mathcal{P})\sigma(t) = e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0)
\]

\[-D(t)(\mathcal{P}\sigma(t) + (1 - \mathcal{P})\sigma(t)\]
Hashitsume-Shibata-Takahashi identity

➤ equation for irrelevant part

\[(1 - \mathcal{P})\sigma(t) = e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0) - i \int_0^t e^{-i(1-\mathcal{P})\mathcal{L}(t-\tau)}(1 - \mathcal{P})\mathcal{L} \mathcal{P} e^{i\mathcal{L}(t-\tau)}\sigma(t) \, d\tau\]

➤ define operator

\[D(t) = i \int_0^t e^{-i(1-\mathcal{P})\mathcal{L}(t-\tau)}(1 - \mathcal{P})\mathcal{L} \mathcal{P} e^{i\mathcal{L}(t-\tau)} \, d\tau\]

\[(1 - \mathcal{P})\sigma(t) = e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0) - D(t)(\mathcal{P}\sigma(t) + (1 - \mathcal{P})\sigma(t))\]

\[(1 + D(t))(1 - \mathcal{P})\sigma(t) = -D(t)\mathcal{P}\sigma(t) + e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0)\]

\[(1 - \mathcal{P})\sigma(t) = (1 + D(t))^{-1} \left( -D(t)\mathcal{P}\sigma(t) + e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)}(1 - \mathcal{P})\sigma(t_0) \right)\]
Hashitsume-Shibata-Takahashi identity

➤ back to first projection

\[
\frac{d}{dt} \mathcal{P} \sigma(t) = -i \mathcal{P} \mathcal{L} \left( \mathcal{P} \sigma(t) + (1 - \mathcal{P}) \sigma(t) \right)
\]

\[
= -i \mathcal{P} \mathcal{L} \left( \mathcal{P} \sigma(t) + (1 + D(t))^{-1} \left( -D(t) \mathcal{P} \sigma(t) + e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)} (1 - \mathcal{P}) \sigma(t_0) \right) \right)
\]

\[
= -i \mathcal{P} \mathcal{L} (1 + D(t))^{-1} \left( \mathcal{P} \sigma(t) + e^{-i(1-\mathcal{P})\mathcal{L}(t-t_0)} (1 - \mathcal{P}) \sigma(t_0) \right)
\]

➤ with

\[
D(t) = i \int_0^t e^{-i(1-\mathcal{P})\mathcal{L}(t-\tau)} (1 - \mathcal{P}) \mathcal{L} \mathcal{P} e^{i\mathcal{L}(t-\tau)} d\tau
\]
Comparison

➤ both identities exact, no approximation so far

➤ Nakajima-Zwanzig identity

\[
\frac{d}{dt} \mathcal{P} \sigma(t) = -i \mathcal{P} \mathcal{L} \mathcal{P} \sigma(t) - \int_{t_0}^{t} \mathcal{P} \mathcal{L} e^{-i(1-\mathcal{P}) \mathcal{L}(t-\tau)} (1 - \mathcal{P}) \mathcal{L} \mathcal{P} \sigma(\tau) d\tau
\]

\[
- i \mathcal{P} \mathcal{L} e^{-i(1-\mathcal{P}) \mathcal{L}(t-t_0)} (1 - \mathcal{P}) \sigma(t_0)
\]

➤ Hashitsume-Shibata-Takahashi identity

\[
\frac{d}{dt} \mathcal{P} \sigma(t) = -i \mathcal{P} \mathcal{L} \left[ 1 + i \int_{0}^{t} e^{-i(1-\mathcal{P}) \mathcal{L} \tau} (1 - \mathcal{P}) \mathcal{L} \mathcal{P} e^{i \mathcal{L} \tau} d\tau \right]^{-1}
\]

\[
\cdot \left[ \mathcal{P} \sigma(t) + e^{-i(1-\mathcal{P}) \mathcal{L}(t-t_0)} (1 - \mathcal{P}) \sigma(t_0) \right]
\]
Projection Operator

➤ Argyres-Kelley projector

\[ \mathcal{P} \ldots = \rho^B \otimes \text{Tr}_B(\ldots), \quad \text{Tr}_B \rho_B = 1 \]

➤ system-plus-bath density matrix

\[ \sigma(t) = \rho^B \otimes \rho(t) \]

➤ \( \rho^B \) equilibrium state of the bath

➤ for simplicity here factorized initial conditions

\[ \sigma(t_0) = \rho^B \otimes \rho(t_0) \]

➤ Hamiltonian \( H = H_S + H_B + H_{S-B} \)

➤ Liouville operators

\[ \mathcal{L}_0 \ldots = \frac{1}{\hbar} [H_0, \ldots] = \mathcal{L}_S + \mathcal{L}_B, \quad \mathcal{L}_1 \ldots = \frac{1}{\hbar} [H_1, \ldots] \propto \lambda \]

\[ H_0 = H_S + H_B, \quad H_1 = H_{S-B} \propto \lambda. \]
second-order in system-bath coupling

\[ \frac{d}{dt} \rho(t) \approx -\frac{i}{\hbar} [H_S, \rho(t)] - \text{Tr}_B \left( \mathcal{L}_1 \int_{t_0}^{t} e^{-i(1-P)\mathcal{L}_0 \cdot \tau} (1-P) \mathcal{L}_1 P e^{i\mathcal{L}_0 \cdot \tau} d\tau (\rho_B \otimes \rho(t)) \right) \]

more identities

\[ P \mathcal{L}_S = \mathcal{L}_S P, \quad \mathcal{P} \mathcal{L}_B = 0 \]

factorized system-bath coupling \( H_{S-B} = \sum_m K_m \Phi_m \)

- \( K_m \) system part
- \( \Phi_m \) bath part

\[ \frac{d}{dt} \rho(t) \approx -\frac{i}{\hbar} [H_S, \rho(t)] - \sum_{m,n} \text{Tr}_B \left( [K_m \Phi_m, \int_{0}^{t} e^{-i(\mathcal{L}_S+\mathcal{L}_B) \tau} \mathcal{L}_1 (\rho_B \otimes e^{i\mathcal{L}_S \tau} \rho_S(t)) d\tau] \right) \]
Time-local approach

➤ reordering within the trace

➤ bath correlation functions

\[ C_{mn}(\tau) = \text{Tr}_B \left( e^{+iH_B \tau} \Phi_m e^{-iH_B \tau} \Phi_n \right) \]

\[ \frac{d}{dt} \rho(t) \approx -\frac{i}{\hbar} [H_S, \rho(t)] - \sum_{m,n} \int_0^t d\tau \left\{ [K_m, e^{-iH_S \tau} K_n e^{iH_S \tau} \rho(t)] C_{mn}(\tau) + [\rho(t) e^{-iH_S \tau} K_n e^{iH_S \tau}, K_m] C^*_{mn}(\tau) \right\} \]

➤ for simplicity: \( H_{S-B} = K \sum_m \Phi_m \)

➤ define operator

\[ \Lambda(t) = \sum_n \int_0^t d\tau C_n(\tau) e^{-iH_S \tau} K_n e^{iH_S \tau} \]
Time-local approach: time-independent Hamiltonian

Define the non-Hermitian effective Hamiltonian

\[ H_{\text{eff}} = H_s + H_{\text{ren}} - iK\Lambda(t) \]

The TL-QME is given by

\[ \frac{\partial \rho(t)}{\partial t} = -i \left( H_{\text{eff}} \rho(t) - \rho(t) H_{\text{eff}}^\dagger \right) + \left( K \rho(t) \Lambda^\dagger(t) + \Lambda(t) \rho K \right) \]

In energy representation

\[ \langle \mu | \Lambda(t) | \nu \rangle = \langle \mu | K | \nu \rangle \int_0^t dt' C(t') e^{-i\omega_{\mu\nu} t'} = \langle \mu | K | \nu \rangle \Theta^+(t, \omega_{\mu\nu}) \]

With

\[ \Theta^+(t, \omega_{\mu\nu}) = \sum_{k=1}^n \frac{p_k}{4\Omega_k \Gamma_k} \left\{ \frac{n_B(\Omega_k^+)}{i(\Omega_k^+ - \omega_{\mu\nu})} \left[ e^{i(\Omega_k^+ - \omega_{\mu\nu}) t} - 1 \right] \right\} - \frac{2i}{\beta} \sum_{k=1}^{n'} \frac{J(i\nu_k)}{\nu_k + i\omega_{\mu\nu}} \left[ e^{(-\nu_k - i\omega_{\mu\nu}) t} - 1 \right] \]

\[ + \frac{n_B(\Omega_k^-) + 1}{i(-\Omega_k^- - \omega_{\mu\nu})} \left[ e^{i(-\Omega_k^- - \omega_{\mu\nu}) t} - 1 \right] \]
Markov approximation and Redfield theory

- simple Markov limit: $\Theta^+(t \to \infty, \omega_{\mu\nu})$

- damping matrix $\Gamma_{\nu\mu,\kappa\lambda}$ for Redfield theory
  \[
  \Gamma_{\nu\mu,\kappa\lambda} = \text{Re} \langle \nu | K | \mu \rangle \langle \kappa | \Lambda(t = \infty) | \lambda \rangle.
  \]

- imaginary part (Lamb shift) is neglected

- at the same time (!) renormalization term is neglected

- neglect of only Lamb shift or only renormalization can cause severe problems

- in Redfield theory influence of time-dependent part of Hamiltonian (laser fields) is neglected (!)
Time-local approach: General formalism

also denoted as time-convolutionless formalism, partial time ordering prescription (POP) or Tokuyama-Mori approach

derived from a second-order cumulant expansion of the time-ordered exponential function

\[
\frac{d \rho(t)}{dt} = -i \mathcal{L}_s \rho(t) + \int_0^t dt' \mathcal{K}(t') \rho(t)
\]

where

\[
\mathcal{K}(t') = \mathcal{L}_- \mathcal{U}_s(t, t') [a(t-t') \mathcal{L}_- - b(t-t') \mathcal{L}_+] \mathcal{U}_s^\dagger(t, t') .
\]

\[
\frac{d \rho(t)}{dt} = -i \mathcal{L}_s^{\text{eff}} \rho(t) + i \mathcal{L}_- \left( [\rho(t), \Lambda^r(t)] + i [\rho(t), \Lambda^i(t)]_+ \right) .
\]

with

\[
\Lambda^r(t) = \int_0^t dt' a(t-t') \mathcal{U}_s(t, t') K, \quad \Lambda^i(t) = \int_0^t dt' b(t-t') \mathcal{U}_s(t, t') K
\]

\[
\mathcal{U}_s(t, t_0) = \mathcal{T}_+ \left[ e^{-i \int_0^t dt'' \mathcal{L}_s(t'')} \right], \quad \mathcal{L}_- = -i [K, \cdot] , \quad \mathcal{L}_+ = [K, \cdot]_+ .
\]
Time-local approach: time-dependent Hamiltonian

➤ define auxiliary operators

\[
\Lambda^r_k(t) = \int_0^t dt' e^{i\gamma^r_k t'} \mathcal{U}_s(t,t') K, \quad \Lambda^i_k(t) = \int_0^t dt' e^{i\gamma^i_k t'} \mathcal{U}_s(t,t') K.
\]

➤ with these expressions the TL-QME can be written as

\[
\frac{d\rho(t)}{dt} = -i \mathcal{L}_s^{\text{eff}} \rho(t) + \mathcal{L} \left( i \sum_{k=1}^{nr} [\rho(t) \Lambda^r_k(t) - \Lambda^r_k(t) \rho(t)] - \sum_{k=1}^{ni} [\rho(t) \Lambda^i_k(t) + \Lambda^i_k(t) \rho(t)] \right)
\]

➤ auxiliary operators \( \Lambda^r_k \) and \( \Lambda^i_k \) can be determined via

\[
\frac{d\Lambda^r_k}{dt} = (\gamma^r_k - i \mathcal{L}_s) \Lambda^r_k + K, \quad \frac{d\Lambda^i_k}{dt} = (\gamma^i_k - i \mathcal{L}_s) \Lambda^r_k + K.
\]
Time-nonlocal approach

➤ often called chronological time ordering prescription (COP), time convolution approach or Mori formalism

➤ based on Nakajima-Zwanzig identity Meier and Tannor developed non-Markovian theory

\[
\frac{d\rho(t)}{dt} = -iL_{\text{eff}}\rho(t) + \int_0^t dt' \mathcal{K}(t,t')\rho(t') + \int_{-\infty}^0 dt' \mathcal{K}(t,t')\rho_{\text{eq}}^B,
\]

where

\[
L_{\text{eff}} = L_s + \frac{\mu}{2}[(K - \phi)^2, \cdot],
\]

\[
\mathcal{K}(t,t') = \mathcal{L}_- \mathcal{U}_s(t,t')[a(t-t')\mathcal{L}_- - b(t-t')\mathcal{L}_+] + \phi = Tr_s(K(q)e^{-\beta H_s})/Tr_s(e^{-\beta H_s})
\]

➤ one can obtain the TL equation by making the approximate substitution

\[
\rho(t') = \mathcal{U}_s^\dagger(t,t')\rho(t)
\]
**Time-nonlocal approach**

- substitute expressions for $a(t)$ and $b(t)$ leads to auxiliary density matrices

\[
\rho^r_k(t) = \int_{-\infty}^t dt' e^{\gamma^r_k(t-t')} \mathcal{U}(t,t') \mathcal{L}_- \rho(t'),
\]

\[
\rho^i_k(t) = \int_{-\infty}^t dt' e^{\gamma^i_k(t-t')} \mathcal{U}(t,t') \mathcal{L}_+ \rho(t').
\]

- master equation can be rewritten as

\[
\dot{\rho}(t) = -i \mathcal{L}^{\text{eff}}_s \rho(t) + \mathcal{L}_- \left\{ \sum_{k=1}^{n_r} \alpha^r_k \rho^r_k(t) - \sum_{k=1}^{n_i} \alpha^i_k \rho^i_k(t) \right\},
\]

\[
\dot{\rho}^r_k(t) = \mathcal{L}_- \rho(t) + (\gamma^r_k - i \mathcal{L}_s) \rho^r_k(t),
\]

\[
\dot{\rho}^i_k(t) = \mathcal{L}_+ \rho(t) + (\gamma^i_k - i \mathcal{L}_s) \rho^i_k(t).
\]
Results for harmonic oscillator: Population dynamics

- Initially all population in the 3rd excited level
- Medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: $\omega_D/\omega_0=2$, $\eta = 0.121$
Results for harmonic oscillator: Population dynamics

➤ initially all population in the 3rd excited level

➤ medium temperature: $\beta = 1/\omega_0$

➤ Drude form, large cut-off: $\omega_D/\omega_0=1$, $\eta = 0.2$
Results for harmonic oscillator: Population dynamics

➤ initially all population in the 3rd excited level

➤ medium temperature: $\beta = 1/\omega_0$

➤ Drude form, large cut-off: $\omega_D/\omega_0=0.5$, $\eta = 0.544$
Results for harmonic oscillator: Population dynamics

- Initially all population in the 3rd excited level
- Medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: $\omega_D/\omega_0=0.5$, $\eta = 0.0544$
Results for harmonic oscillator: Variance of $q$

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: $\omega_D/\omega_0=0.5$, $\eta = 0.544$
Results for harmonic oscillator: Variance of $q$

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: $\omega_D/\omega_0=0.5$, $\eta = 0.544$
Results for harmonic oscillator: Low Temperature

- Initially all population in the 3rd excited level
- Low temperature: $\beta = \frac{100}{\omega_0}$
- Drude form, large cut-off: $\omega_D / \omega_0 = 0.5$, $\eta = 0.544$
References


➤ Xu, Yan, Ohtsuki, Fujimura, Rabitz, J. Chem. Phys. 120, 6600 (2004)