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

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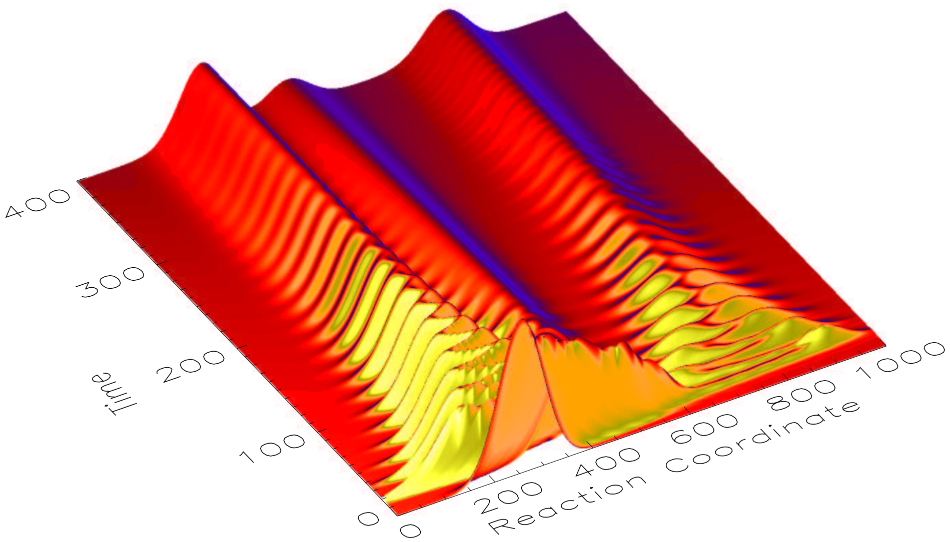


Overview

- 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

$$
\begin{aligned}
i\hbar\frac{d\sigma(t)}{dt} &= i\hbar\frac{d|\Psi\rangle\langle\Psi|}{dt} = i\hbar\left(\frac{|d\Psi\rangle}{dt}\langle\Psi| + |\Psi\rangle\frac{\langle d\Psi|}{dt}\right) \\
&= [H(t), \sigma(t)]
\end{aligned}
$$

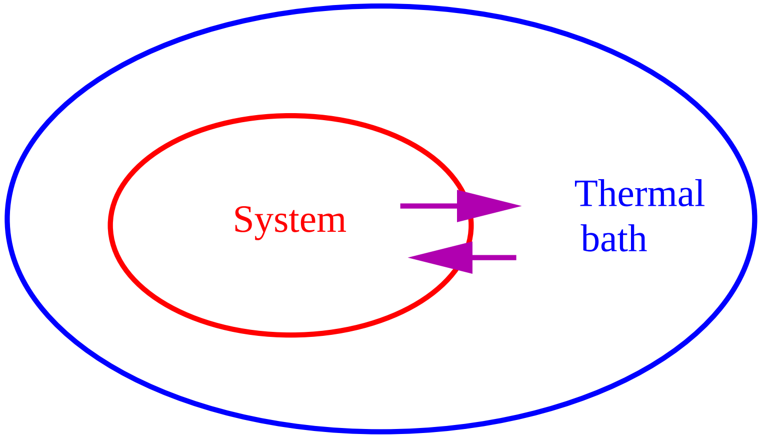
- observables:

$$
\begin{aligned}
\langle Q\rangle = \langle\Psi|Q|\Psi\rangle &= \sum_n \langle\Psi|n\rangle\langle n|Q|\Psi\rangle \\
&= \sum_n \langle n|Q|\Psi\rangle\langle\Psi|n\rangle = tr(Q\sigma)
\end{aligned}
$$

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

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

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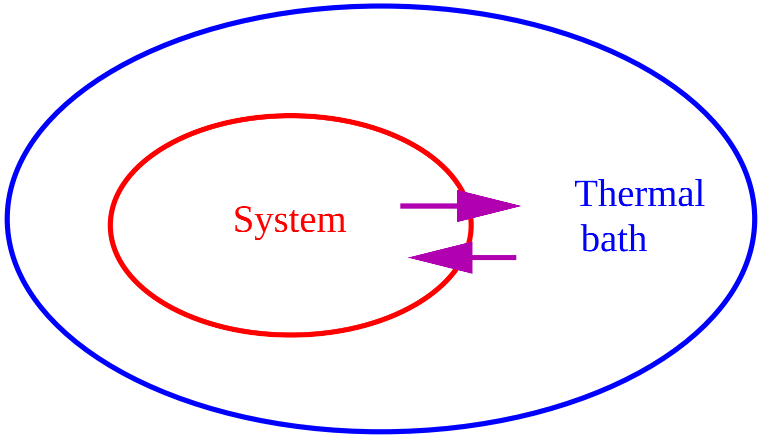

- reduced density matrix approach:
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  $\rho = tr_B(\sigma)$ - density matrix of the relevant system

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

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 $x_i = \frac{c_i K(q)}{m_i \omega_i^2}$
  - for $K(q) = q$ leads to shift $\Delta\omega^2 = -\sum_i c_i^2/(M m_i \omega_i^2)$
  - 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

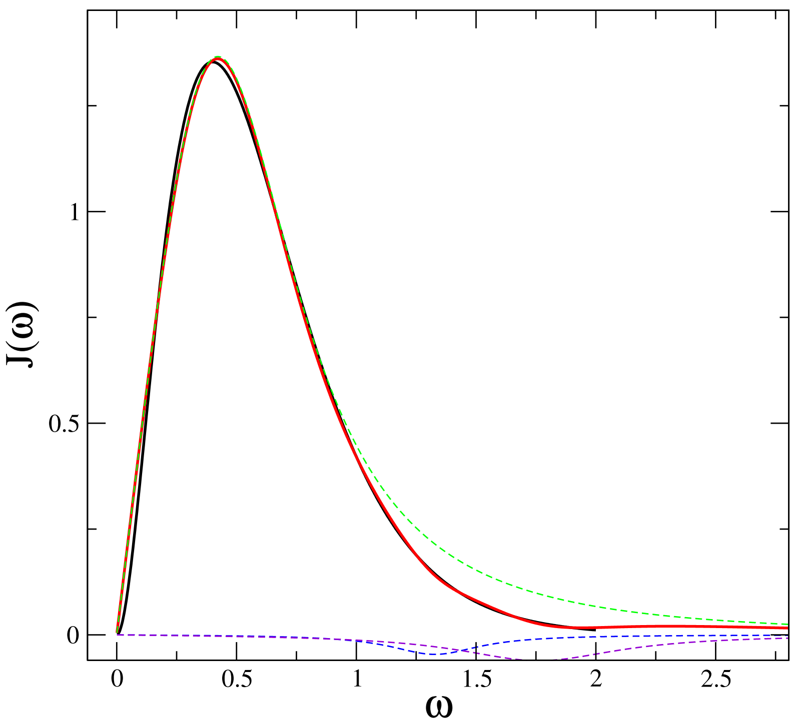
$$J(\omega) = \frac{\pi}{2}\sum_i \frac{c_i^2}{m_i\omega_i}\delta(\omega-\omega_i)$$

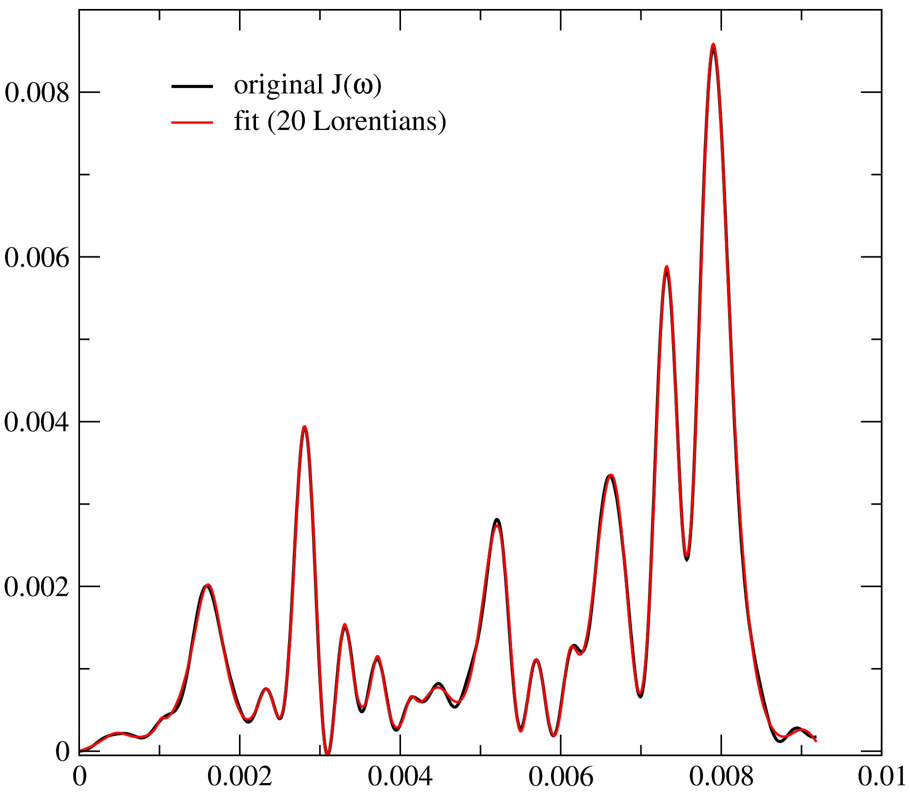
- property $J(-\omega) = -J(\omega)$

- numerical decomposition in Lorentzians (Meier and Tannor)

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

Decomposition of the spectral density





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

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

with

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

and

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

- 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 $i\frac{d}{dt}\sigma(t) = \mathscr{L}\sigma(t)$ with $\mathscr{L}\ldots = \frac{1}{\hbar}[H,\ldots]$
- for simplicity here H time-independent
- use projector P onto relevant part of the whole system, $\mathscr{P}+\mathscr{Q}=1$, $\mathscr{P}=\mathscr{P}^2$
- project onto relevant and irrelevant part

$$
\begin{aligned}
i\frac{d}{dt}\mathscr{P}\sigma(t) &= \mathscr{P}\mathscr{L}\sigma(t) = \mathscr{P}\mathscr{L}\mathscr{P}\sigma(t) + \mathscr{P}\mathscr{L}(1-\mathscr{P})\sigma(t) \\
i\frac{d}{dt}(1-\mathscr{P})\sigma(t) &= (1-\mathscr{P})\mathscr{L}\sigma(t) = (1-\mathscr{P})\mathscr{L}\mathscr{P}\sigma(t) + (1-\mathscr{P})\mathscr{L}(1-\mathscr{P})\sigma(t)
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\end{aligned}
$$

- solve equation for the irrelevant part

$$
(1-\mathscr{P})\sigma(t) = \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t)}(1-\mathscr{P})\sigma(t_0) - i\int_0^t \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\sigma(\tau)\,d\tau
$$

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$$

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

$$
\begin{aligned}
\frac{d}{dt}\mathscr{P}\sigma(t) &= -i\mathscr{P}\mathscr{L}\mathscr{P}\sigma(t) - \int_0^t \mathscr{P}\mathscr{L}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\sigma(\tau)\,d\tau \\
&\quad -i\mathscr{P}\mathscr{L}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\sigma(t_0)
\end{aligned}
$$

Hashitsume-Shibata-Takahashi identity

- equation for irrelevant part

$$
\begin{aligned}
(1-\mathscr{P})\boldsymbol{\sigma}(t) &= \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\boldsymbol{\sigma}(t_0) \\
&\quad -i\int_0^t \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\mathrm{e}^{i\mathscr{L}(t-\tau)}\boldsymbol{\sigma}(t)\,d\tau
\end{aligned}
$$

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\end{aligned}
$$

- define operator

$$
D(t) = i\int_0^t \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\mathrm{e}^{\mathrm{i}\mathscr{L}(t-\tau)}\,d\tau
$$

$$
\begin{aligned}
(1-\mathscr{P})\sigma(t) &= \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-0)}(1-\mathscr{P})\sigma(t_0) \\
&\quad -D(t)(\mathscr{P}\sigma(t)+(1-\mathscr{P})\sigma(t)
\end{aligned}
$$

Hashitsume-Shibata-Takahashi identity

- equation for irrelevant part

$$
\begin{aligned}
(1-\mathscr{P})\sigma(t) &= e^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\sigma(t_0) \\
&\quad -i\int_0^t e^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}e^{i\mathscr{L}(t-\tau)}\sigma(t)\,d\tau
\end{aligned}
$$

- define operator

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D(t) = i\int_0^t e^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}e^{i\mathscr{L}(t-\tau)}\,d\tau
$$

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(1-\mathscr{P})\sigma(t) &= e^{-i(1-\mathscr{P})\mathscr{L}(t-0)}(1-\mathscr{P})\sigma(t_0) \\
&\quad -D(t)(\mathscr{P}\sigma(t)+(1-\mathscr{P})\sigma(t)
\end{aligned}
$$

$$
(1+D(t))(1-\mathscr{P})\sigma(t) = -D(t)\mathscr{P}\sigma(t) + e^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\sigma(t_0)
$$

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

Hashitsume-Shibata-Takahashi identity

- back to first projection

$$\begin{aligned}\frac{d}{dt}\mathscr{P}\boldsymbol{\sigma}(t) &= -i\mathscr{P}\mathscr{L}\left(\mathscr{P}\boldsymbol{\sigma}(t)+(1-\mathscr{P})\boldsymbol{\sigma}(t)\right)\\ &= -i\mathscr{P}\mathscr{L}\left(\mathscr{P}\boldsymbol{\sigma}(t)+(1+D(t))^{-1}\left(-D(t)\mathscr{P}\boldsymbol{\sigma}(t)+\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\boldsymbol{\sigma}(t_0)\right)\right)\\ &= -i\mathscr{P}\mathscr{L}(1+D(t))^{-1}\left(\mathscr{P}\boldsymbol{\sigma}(t)+\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\boldsymbol{\sigma}(t_0)\right)\end{aligned}$$

- with

$$D(t)=i\int_0^t \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\mathrm{e}^{i\mathscr{L}(t-\tau)}\,d\tau$$

Comparison

- both identities exact, no approximation so far
- Nakajima-Zwanzig identity

$$\frac{d}{dt}\mathscr{P}\boldsymbol{\sigma}(t) = -i\mathscr{P}\mathscr{L}\mathscr{P}\boldsymbol{\sigma}(t) - \int_{t_0}^{t}\mathscr{P}\mathscr{L}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-\tau)}(1-\mathscr{P})\mathscr{L}\mathscr{P}\boldsymbol{\sigma}(\tau)\,d\tau$$
$$-i\mathscr{P}\mathscr{L}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\boldsymbol{\sigma}(t_0)$$

- Hashitsume-Shibata-Takahashi identity

$$\frac{d}{dt}\mathscr{P}\boldsymbol{\sigma}(t) = -i\mathscr{P}\mathscr{L}[1+i\int_{0}^{t}\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}\tau}(1-\mathscr{P})\mathscr{L}\mathscr{P}\mathrm{e}^{i\mathscr{L}\tau}\,d\tau]^{-1}$$
$$\cdot[\mathscr{P}\boldsymbol{\sigma}(t)+\mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}(t-t_0)}(1-\mathscr{P})\boldsymbol{\sigma}(t_0)]$$

Projection Operator

- Argyres-Kelley projector

$$\mathscr{P}\ldots = \rho^B \otimes \mathrm{Tr}_B(\ldots), \quad \mathrm{Tr}_B \rho_B = 1$$

- system-plus-bath density matrix

$$\sigma(t) = \rho^B \otimes \rho(t)$$

- ρ^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

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

$$H_0 = H_S + H_B, \quad H_1 = H_{S-B} \propto \lambda.$$

Time-local approach

- second-order in system-bath coupling

$$\frac{d}{dt}\rho(t) \approx -\frac{i}{\hbar}[H_S,\rho(t)] - \mathrm{Tr}_B\left(\mathscr{L}_1\int_0^{t-t_0} \mathrm{e}^{-i(1-\mathscr{P})\mathscr{L}_0\cdot\tau}(1-\mathscr{P})\mathscr{L}_1\mathscr{P}\mathrm{e}^{i\mathscr{L}_0\cdot\tau}d\tau\,(\rho^B\otimes\rho(t))\right)$$

- more identities

$$\mathscr{P}\mathscr{L}_S = \mathscr{L}_S\mathscr{P}, \qquad \mathscr{P}\mathscr{L}_B = 0$$

$$\frac{d}{dt}\rho(t) \approx -\frac{i}{\hbar}[H_S,\rho(t)] - \mathrm{Tr}_B\left(\mathscr{L}_1\int_0^{t} \mathrm{e}^{-i(\mathscr{L}_S+\mathscr{L}_B)\tau}\mathscr{L}_1(\rho^B\otimes\mathrm{e}^{i\mathscr{L}_S\tau}\rho_S(t))d\tau\right)$$

- factorized system-bath coupling $H_{S-B} = \sum_m K_m\Phi_m$
  - K_m system part
  - Φ_m bath part

$$\frac{d}{dt}\rho(t) \approx -\frac{i}{\hbar}[H_S,\rho(t)] - \sum_{m,n}\mathrm{Tr}_B\left([K_m\Phi_m,\int_0^{t} \mathrm{e}^{-i(\mathscr{L}_S+\mathscr{L}_B)\tau}[K_n\Phi_n,(\rho^B\otimes\mathrm{e}^{i\mathscr{L}_S\tau}\rho_S(t))]]d\tau\right)$$

Time-local approach

- reordering within the trace
- bath correlation functions

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

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

- for simplicity: $H_{S-B} = K \sum_m \Phi_m$
- define operator

$$\Lambda(t) = \sum_n \int_0^t d\tau C_n(\tau) \mathrm{e}^{-iH_S\tau} K_n \mathrm{e}^{iH_S\tau}$$

Time-local approach: time-independent Hamiltonian

- define the non-Hermitian effective Hamiltonian

$$H_{\text{eff}} = H_{\text{s}} + H_{\text{ren}} - iK\Lambda(t)$$

- 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

$$\Theta^{+}(t,\omega_{\mu\nu}) = \sum_{k=1}^{n} \frac{p_k}{4\Omega_k\Gamma_k}\left\{\frac{n_B(\Omega_k^{+})}{i(\Omega_k^{+}-\omega_{\mu\nu})}\left[e^{i(\Omega_k^{+}-\omega_{\mu\nu})t}-1\right]\right.$$

$$\left. + \quad \frac{[n_B(\Omega_k^{-})+1]}{i(-\Omega_k^{-}-\omega_{\mu\nu})}\left[e^{i(-\Omega_k^{-}-\omega_{\mu\nu})t}-1\right]\right\} - \frac{2i}{\beta}\sum_{k=1}^{n'} \frac{J(i\nu_k)}{\nu_k+i\omega_{\mu\nu}}\left[e^{(-\nu_k-i\omega_{\mu\nu})t}-1\right]$$

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

$$\Gamma_{\nu\mu,\kappa\lambda} = \mathrm{Re}\langle \nu|K|\mu\rangle\langle\kappa|\Lambda(t=\infty)|\lambda\rangle \ .$$

- 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-convoulutionless formalism, partial time ordering prescription (POP) or Tokuyama-Mori approach

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

$$\frac{d\rho(t)}{dt} = -i\mathscr{L}_s^{\text{eff}}\rho(t) + \int_0^t dt' \mathscr{K}(t')\rho(t)$$

where

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

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

with

$$\Lambda^r(t) = \int_0^t dt' a(t-t')\mathscr{U}_s(t,t')K, \ \ \Lambda^i(t) = \int_0^t dt' b(t-t')\mathscr{U}_s(t,t')K$$

$$\mathscr{U}_s(t,t_0) = \mathscr{T}_+\left[e^{-i\int_{t_0}^t dt'' \mathscr{L}_s(t'')}\right] \ , \ \mathscr{L}_- = -i[K,\cdot] \ , \ \mathscr{L}_+ = [K,\cdot]_+ \ ,$$

Time-local approach: time-dependent Hamiltonian

- define auxiliary operators

$$\Lambda_k^r(t) = \int_0^t dt' e^{\gamma_k^r t'} \mathscr{U}_s(t,t')K, \qquad \Lambda_k^i(t) = \int_0^t dt' e^{\gamma_k^i t'} \mathscr{U}_s(t,t')K \ .$$

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

$$\begin{aligned} \frac{d\rho(t)}{dt} = -i\mathscr{L}_s^{\text{eff}}\rho(t) \quad &+ \quad \mathscr{L}_- \Bigg(i \sum_{k=1}^{n_r} [\rho(t)\Lambda_k^r(t) - \Lambda_k^r(t)\rho(t)] \\ &- \quad \sum_{k=1}^{n_i} [\rho(t)\Lambda_k^i(t) + \Lambda_k^i(t)\rho(t)] \Bigg) \end{aligned}$$

- auxiliary operators Λ_k^r and Λ_k^i can be determined via

$$\frac{d\Lambda_k^r}{dt} = (\gamma_k^r - i\mathscr{L}_s)\Lambda_k^r + K, \qquad \frac{d\Lambda_k^i}{dt} = (\gamma_k^i - i\mathscr{L}_s)\Lambda_k^r + K \ .$$

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

$$\frac{d\rho(t)}{dt} = -i\mathscr{L}_s^{\text{eff}}\rho(t) + \int_0^t dt'\mathscr{K}(t,t')\rho(t') + \int_{-\infty}^0 dt'\mathscr{K}(t,t')\rho_B^{eq} \ ,$$

where

$$\begin{aligned}
\mathscr{L}_s^{\text{eff}} &= \mathscr{L}_s + \frac{\mu}{2}[(K-\phi)^2,\cdot] \ , \\
\mathscr{K}(t,t') &= \mathscr{L}_-\mathscr{U}_s(t,t')[a(t-t')\mathscr{L}_- - b(t-t')\mathscr{L}_+] \\
\phi &= Tr_s(K(q)e^{-\beta H_s})/Tr_s(e^{-\beta H_s})
\end{aligned}$$

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

$$\rho(t') = \mathscr{U}_s^\dagger(t,t')\rho(t)$$

Time-nonlocal approach

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

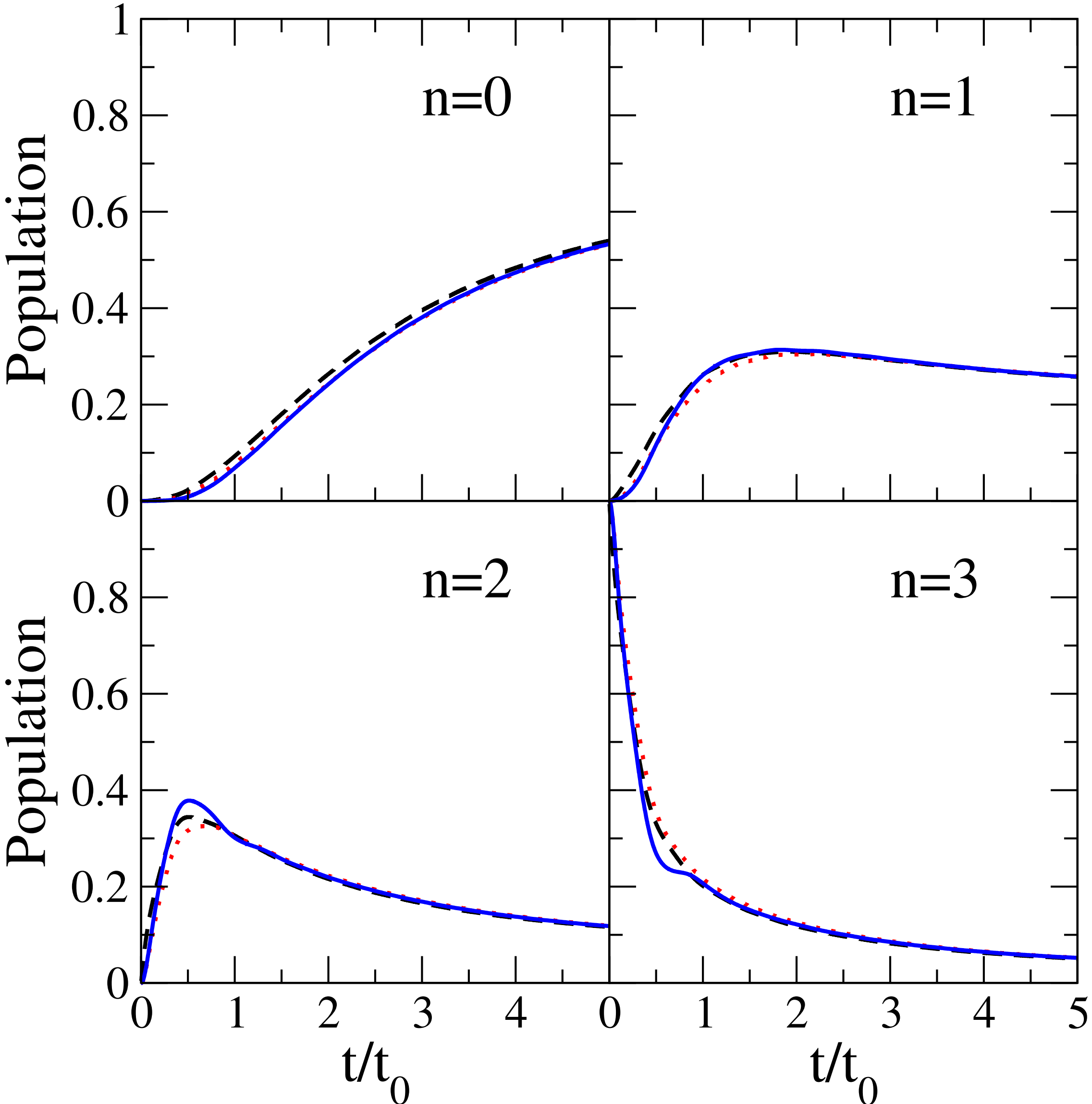
$$
\begin{aligned}
\rho_k^r(t) &= \int_{-\infty}^{t} dt' e^{\gamma_k^r (t-t')} \mathcal{U}(t,t') \mathcal{L}_- \rho(t') \; , \\
\rho_k^i(t) &= \int_{-\infty}^{t} dt' e^{\gamma_k^i (t-t')} \mathcal{U}(t,t') \mathcal{L}_+ \rho(t') \; .
\end{aligned}
$$

- master equation can be rewritten as

$$
\begin{aligned}
\dot{\rho}(t) &= -i\mathcal{L}_s^{\mathrm{eff}} \rho(t) + \mathcal{L}_- \left\{ \sum_{k=1}^{n_r} \alpha_k^r \rho_k^r(t) - \sum_{k=1}^{n_i} \alpha_k^i \rho_k^i(t) \right\} \; , \\
\dot{\rho}_k^r(t) &= \mathcal{L}_- \rho(t) + (\gamma_k^r - i\mathcal{L}_s) \rho_k^r(t) \\
\dot{\rho}_k^i(t) &= \mathcal{L}_+ \rho(t) + (\gamma_k^i - i\mathcal{L}_s) \rho_k^i(t) \; .
\end{aligned}
$$

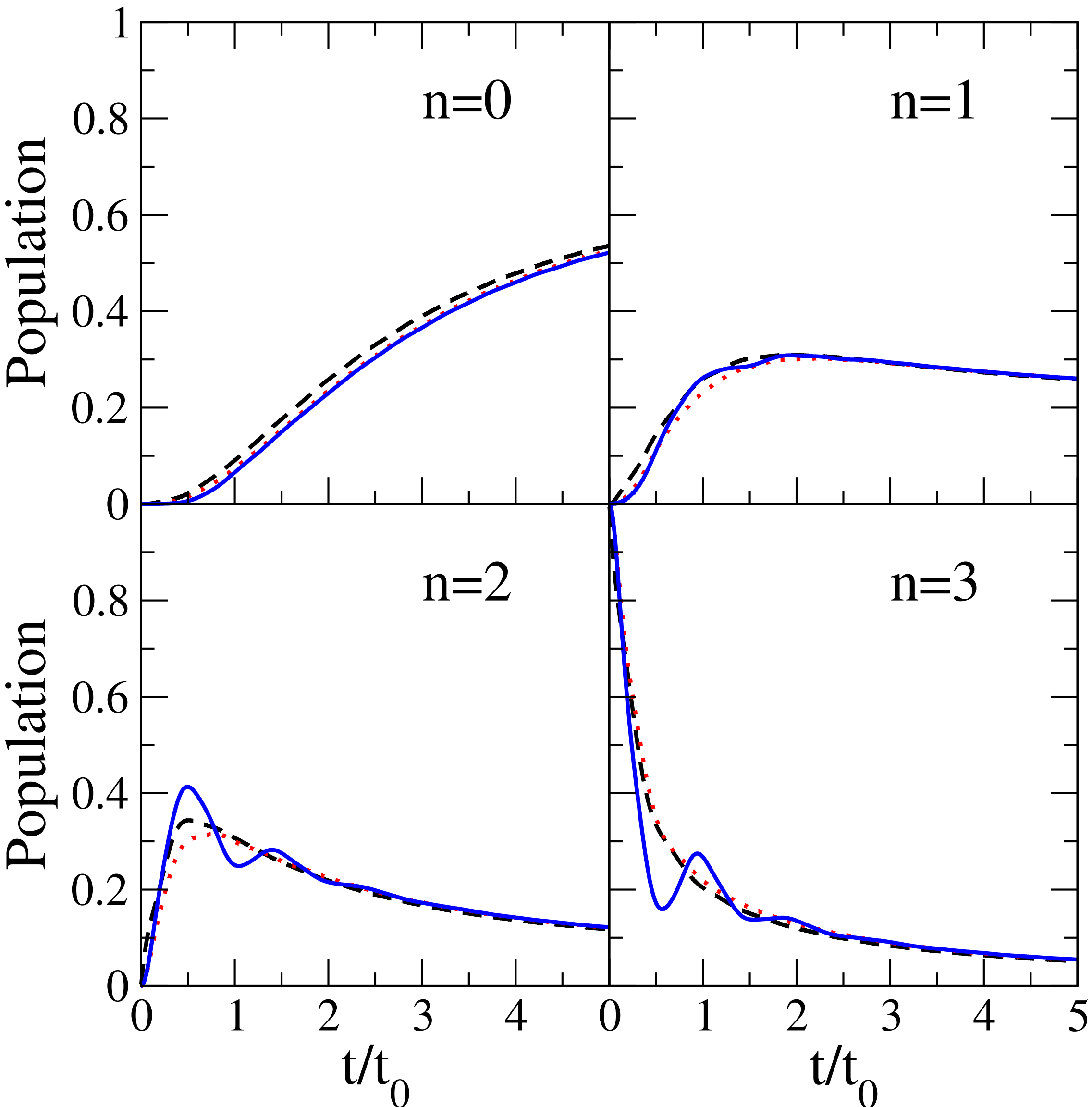
Results for harmonic oscillator: Population dynamics

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=2, $\eta = 0.121$



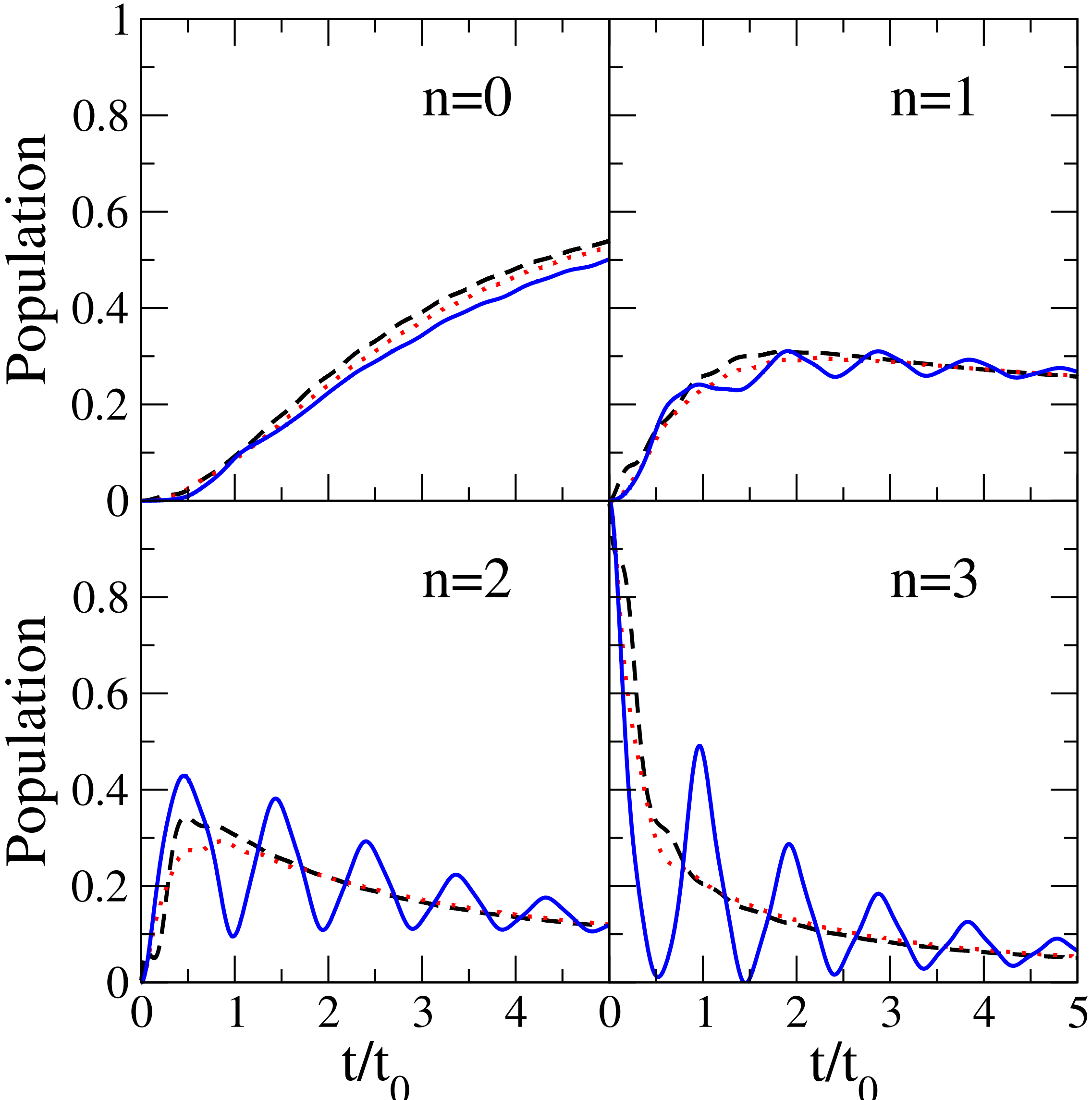
Results for harmonic oscillator: Population dynamics

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=1, $\eta = 0.2$



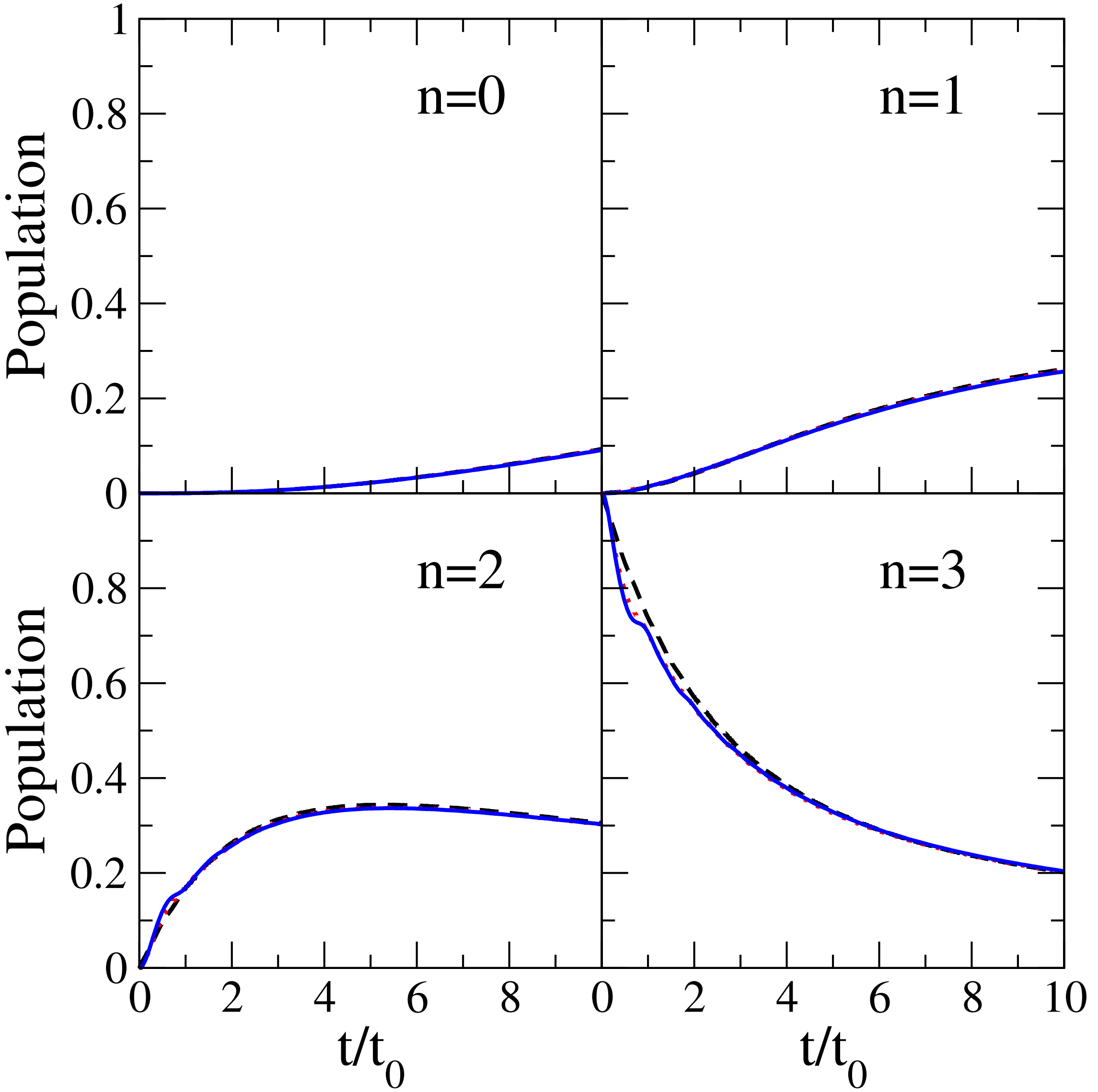
Results for harmonic oscillator: Population dynamics

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=0.5, $\eta = 0.544$



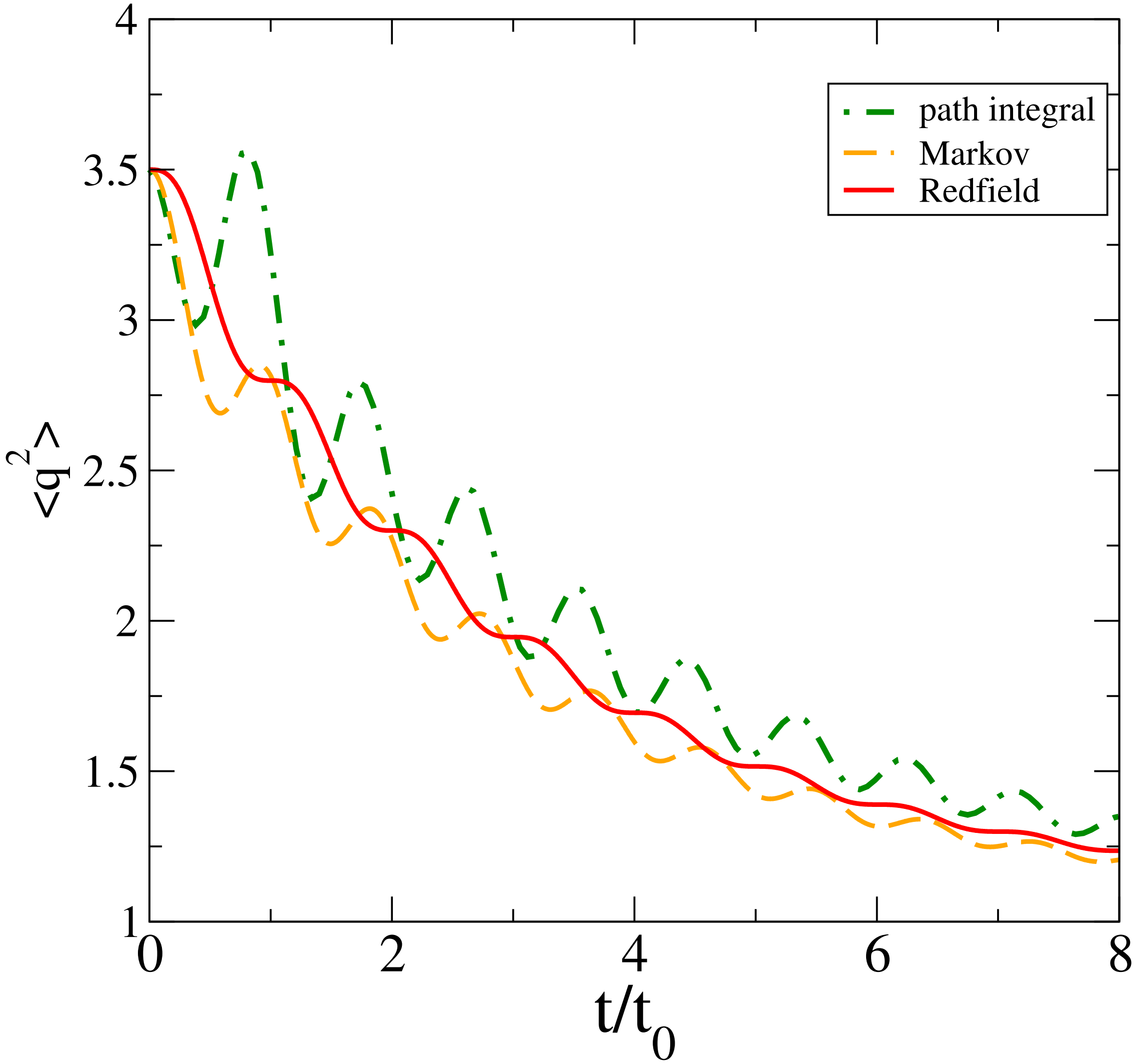
Results for harmonic oscillator: Population dynamics

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=0.5, $\eta = 0.0544$



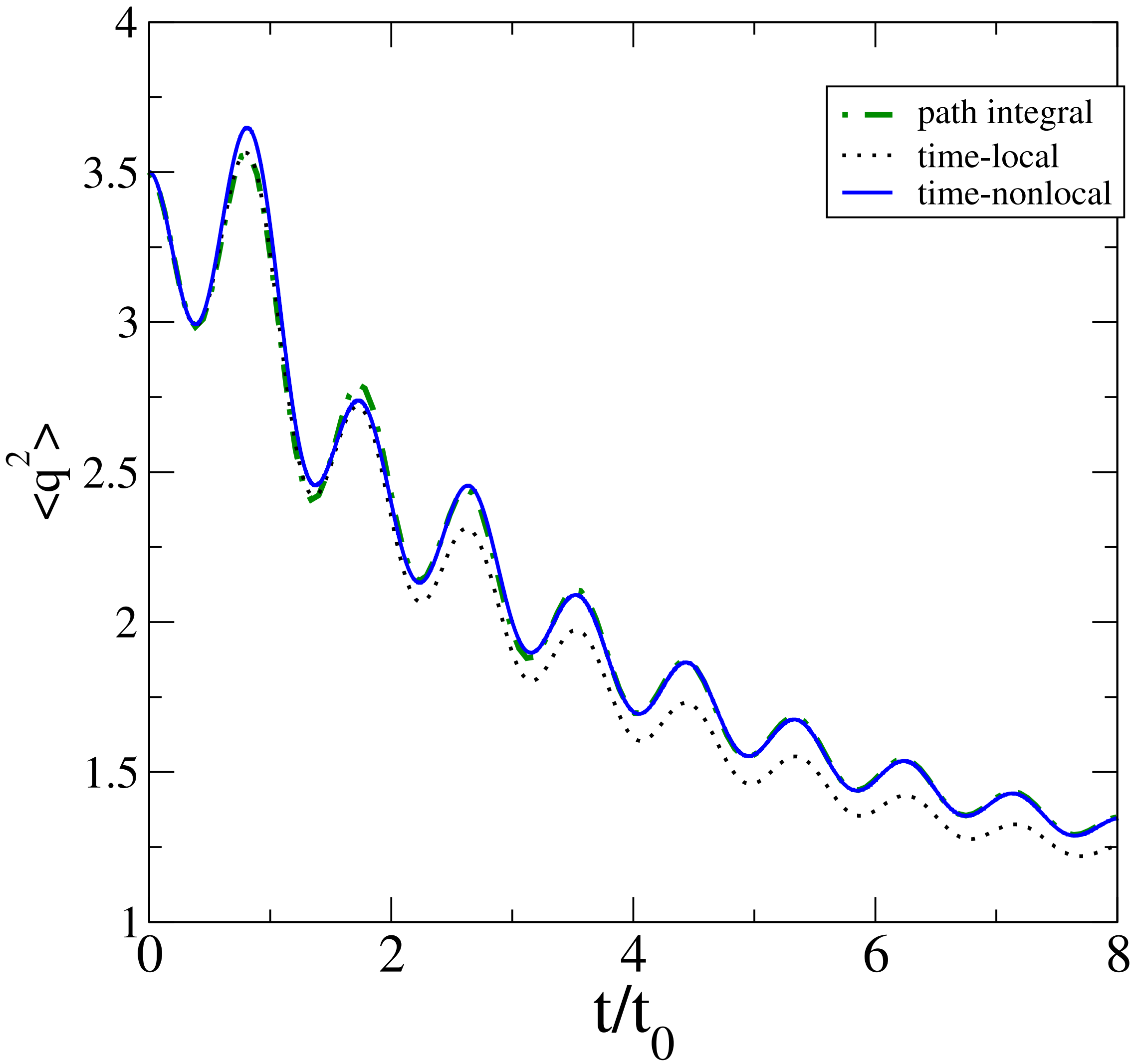
Results for harmonic oscillator: Variance of q

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=0.5, $\eta = 0.544$



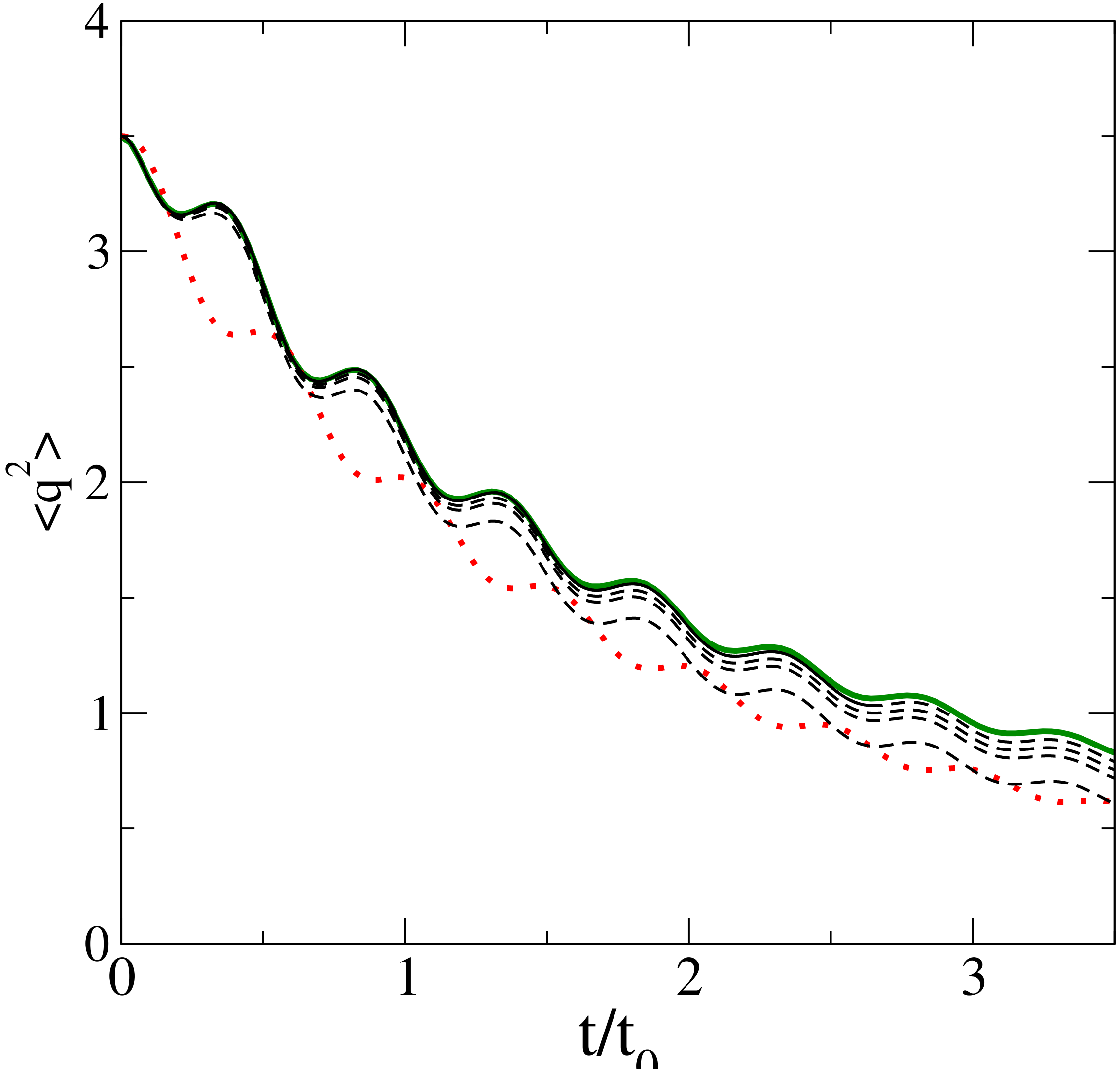
Results for harmonic oscillator: Variance of q

- initially all population in the 3rd excited level
- medium temperature: $\beta = 1/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=0.5, $\eta = 0.544$



Results for harmonic oscillator: Low Temperature

- initially all population in the 3rd excited level
- low temperature: $\beta = 100/\omega_0$
- Drude form, large cut-off: ω_D/ω_0=0.5, $\eta = 0.544$



References

- Meier, Tannor, J. Chem. Phys. **111**, 3365 (1999)
- Kleinekathöfer, J. Chem. Phys. **121**, 2505 (2004)
- Xu, Yan, J. Chem. Phys. **116**, 9196 (2002)
- Xu, Yan, Ohtsuki, Fujimura, Rabitz, J. Chem. Phys. **120**, 6600 (2004)
- Breuer, Burgarth, Petruccione, Phys. Rev. B **70**, 045323 (2004)