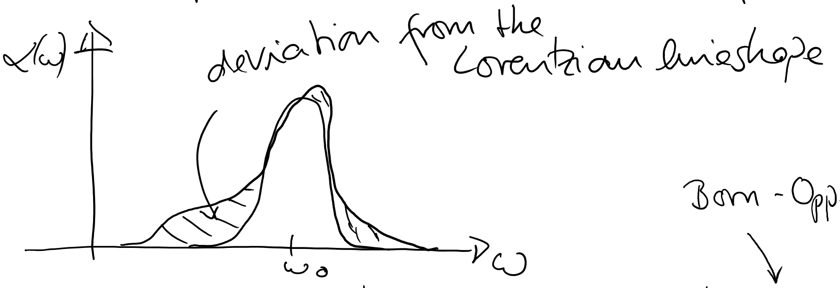
an analytically solvable model for a trivial system Hamiltonian but it allows to model accurately absorption spectra, and therefore it increases the understanding of lineshapes and timescale of material systems.

—— $|1\rangle$

—— $|0\rangle$

$\sigma_{11} = |1\rangle\langle 1|$



Born-Oppenheimer

Hamiltonian: $H = \hbar\omega_0 \sigma_{11} + \sum_q \hbar\omega_q r_q^\dagger r_q + \sum_q \hbar g_q (r_q + r_q^\dagger)\sigma_{11}$

(spin-boson problem)

Interaction $H_I(t) = \hbar \sum_q g_q [r_q(t) + r_q^\dagger(t)]\, \sigma_{11}$ (no dynamical phase)

first choice, master equation

$$\dot\rho_s = -\frac{i}{\hbar}[\hbar\omega_0\sigma_{11}, \rho_s] - \int_0^t d\tau \Big\{ \langle R^\dagger R(-\tau)\rangle \left(J J^\dagger(-\tau)\rho_s - J^\dagger(-\tau)\rho_s J\right)$$
$$+ \langle R^\dagger(-\tau) R\rangle \left(\rho_s J(-\tau) J^\dagger - J^\dagger \rho_s J(-\tau)\right)$$
$$+ \langle R R^\dagger(-\tau)\rangle \left(J^\dagger J(-\tau)\rho_s - J(-\tau)\rho_s J^\dagger\right)$$
$$+ \langle R(-\tau) R^\dagger\rangle \left(\rho_s J^\dagger(-\tau) J - J\rho_s J^\dagger(-\tau)\right)\Big\}$$

$$J(t) = \sigma_{11} = J^\dagger(t)$$
$$\langle R R^\dagger(-\tau)\rangle = \sum_q |g_q|^2 e^{-i\omega_q\tau}(\bar n_q + 1)$$

$$\dot\rho_s = -i[\omega_0\sigma_{11}, \rho_s] - \sum_q |g_q|^2 \int_0^t d\tau \Big\{ \bar n_q e^{i\omega_q\tau}(\sigma_{11}\rho_s - \sigma_{11}\rho_s\sigma_{11})$$
$$+ \bar n_q e^{-i\omega_q\tau}(\rho_s\sigma_{11} - \sigma_{11}\rho_s\sigma_{11})$$
$$+ (\bar n_q + 1) e^{-i\omega_q\tau}(\sigma_{11}\rho_s - \sigma_{11}\rho_s\sigma_{11})$$
$$+ (\bar n_q + 1) e^{i\omega_q\tau}(\rho_s\sigma_{11} - \sigma_{11}\rho_s\sigma_{11})\Big\}$$

$$= -i[\omega_0\sigma_{11}, \rho_s] - \sum_q |g_q|^2 (\sigma_{11}\rho_s - \sigma_{11}\rho_s\sigma_{11}) \int_0^t d\tau \left(\bar n_q e^{i\omega_q\tau} + (\bar n_q + 1)e^{-i\omega_q\tau}\right)$$
$$- \sum_q |g_q|^2 (\rho_s\sigma_{11} - \sigma_{11}\rho_s\sigma_{11}) \int_0^t d\tau \left(\bar n_q e^{-i\omega_q\tau} + (\bar n_q + 1)e^{i\omega_q\tau}\right)$$

$\rightarrow$ apply second Markovian approximation $\int_0^t d\tau \rightarrow \int_0^\infty d\tau$

$$\approx -i[\omega_0 \sigma_{11}, \rho_S] - \sum_k' \underbrace{|g_k|^2 (2\bar{n}_k + 1)\,\delta(\omega_k)}\,[2\sigma_{11}\rho_S\sigma_{11} - \sigma_{11}\rho_S - \rho_S\sigma_{11}]$$

very problematic for $T>0$
since $\bar{n}_k \to \infty$ for $\omega_k \to 0$

but if $T=0$, $\bar{n}_k = 0$
then $\sum_k |g_k|^2 \delta(\omega_k) = \int d\omega\, J(\omega)\, \delta(\omega)$
then it contributes for $J(\omega) = \text{const.}$
and is vanishes for $J(\omega) = \omega^s$, $s>1$
and it diverges for $J(\omega) = \omega^s$, $s<1$

$\Rightarrow$ there prime example to use non-perturbative propagator method, since Markovian master equation fails for spin-boson model in the presence of super-ohmic environments
$J(\omega) \sim \omega^s$, $s>1$ (typically phonons show $s=3$)

$$\dot{\rho}_I = -\frac{i}{\hbar}[H_I(t), \rho_I(t)] \longrightarrow \rho_I(t) = \hat{T}\left\{\exp\left[\int_0^t dt'\, \mathcal{L}_I(t')\right]\rho_I(0)\right\}$$

What we need to do is to find the Feynman-Vernon influence functional

2nd order $\mathrm{tr}_B\left\{-\frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2\, \mathcal{L}_I(t_1)\mathcal{L}_I(t_2)\rho_I(0)\right\}$

$$\mathcal{L}_I(t_1)\mathcal{L}_I(t_2)\rho_I(0) = [H_I(t_1), \sigma_{11}(B(t_2)+B^+(t_2))\rho_I(0) - \rho_I(0)(B(t_2)+B^+(t_2))\sigma_{11}]$$

$$\begin{aligned}
= \ & \sigma_{11}B^+(t_1)B(t_2)\rho_I(0) - \sigma_{11}B(t_2)\rho_I(0)B^+(t_1)\sigma_{11} \\
& + \sigma_{11}B(t_1)B^+(t_2)\rho_I(0) - \sigma_{11}B^+(t_2)\rho_I(0)B(t_1)\sigma_{11} \\
& - \sigma_{11}B^+(t_1)\rho_I(0)B(t_2)\sigma_{11} + \rho_I(0)B(t_2)B^+(t_1)\sigma_{11} - \sigma_{11}B(t_1)\rho_I(0)B^+(t_2)\sigma_{11} \\
& + \rho_I(0)B^+(t_2)B(t_1)\sigma_{11}
\end{aligned}$$

$$\mathrm{tr}_B\{\mathcal{L}_I(t_1)\mathcal{L}_I(t_2)\rho_I(0)\} =$$

$$\begin{aligned}
= \ & \sigma_{11}\rho_S(0)(\langle B_1^+B_2\rangle + \langle B_1B_2^+\rangle) - \sigma_{11}\rho_S^{(0)}\sigma_{11}(\langle B_1^+B_2\rangle + \langle B_2B_1^+\rangle \\
& \qquad + \langle B_2^+B_1\rangle + \langle B_1B_2^+\rangle) \\
& + \rho_S(0)\sigma_{11}(\langle B_2B_1^+\rangle + \langle B_2^+B_1\rangle)
\end{aligned}$$

$$\langle B_1^+B_2\rangle = \sum_k |g_k|^2 e^{i\omega_k(t_1-t_2)}\,\bar{n}_k$$

$$\langle B_1^+ B_2 \rangle = \sum_k |g_k|^2 e^{i\omega_k(t_1-t_2)} \overline{n_k}$$

$$\langle B_2 B_1^+ \rangle = \sum_k |g_k|^2 e^{-i\omega_k(t_1-t_2)} (\overline{n_k}+1)$$

$$\langle B_1^+ B_2 \rangle + \langle B_1 B_2^+ \rangle = \sum_k |g_k|^2 \Big\{ \coth\Big[\frac{\hbar\omega_k}{2k_B T}\Big] \cos[\omega_k(t_1-t_2)] - i \sin[\omega_k(t_1-t_2)] \Big\}$$

$$= D_c(t_1-t_2) - i D_s(t_1-t_2)$$ (thermal equilibrium in the bath)

$$\mathrm{tr}_B\{\mathcal{L}_I(t_1)\mathcal{L}_I(t_2)\rho_I(0)\} = D_c(t_1-t_2)[\sigma_{11}\rho_S(0)+\rho_S(0)\sigma_{11}]$$
$$-i D_s(t_1-t_2)[\sigma_{11}\rho_S(0)-\rho_S(0)\sigma_{11}]$$
$$-2\sigma_{11}\rho_S\sigma_{11} D_c(t_1-t_2)$$

$$\int_0^t dt_1 \int_0^{t_1} dt_2\, D_c(t_1-t_2) = \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_k |g_k|^2 \coth\Big[\frac{\hbar\omega_k}{2k_BT}\Big]\cos[\omega_k(t_1-t_2)]$$

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \cos[\omega_k(t_1-t_2)] = \mathrm{Re}\Big[\int_0^t dt_1 \int_0^{t_1} dt_2\, e^{i\omega_k(t_1-t_2)}\Big]$$

$$= \mathrm{Re}\Big[\int_0^t dt_1\, e^{i\omega_k t_1} \frac{e^{-i\omega_k t_1}-1}{-i\omega_k}\Big] = \ldots = \frac{1}{\omega_k^2}[1-\cos\omega_k t]$$

$$\mathrm{Im}\Big[\int_0^t dt_1 \int_0^{t_1} dt_2\, e^{i\omega_k t_1 - i\omega_k t_2}\Big] = \ldots = \frac{t}{\omega_k} - \frac{\sin\omega_k}{\omega_k^2} \quad //$$

<u>hence</u>: $D_c(t_1-t_2)\{-2\sigma_{11}\rho_S(0)\sigma_{11}+\sigma_{11}\rho_S(0)+\rho_S(0)\sigma_{11}\}$

$$-iD_s(t_1-t_2)\{\sigma_{11}\rho_S(0)-\rho_S(0)\sigma_{11}\}$$

$$= -D_c(t_1-t_2)\,\mathcal{D}[\sigma_{11}]\rho_S(0) - iD_s(t_1-t_2)\,\mathcal{L}[\sigma_{11}]\rho_S(0)$$

with $\mathcal{D}[J]\rho := 2J\rho J^+ - J^+J\rho - \rho J^+ J$ (Lindblad)

$\mathcal{L}[J]\rho := [J,\rho]$ (Liouvillian)

$$\int_0^t dt_1 \int_0^{t_1} dt_2\, \mathrm{tr}_B\{\mathcal{L}_I(t_1)\mathcal{L}_I(t_2)\rho_I(0)\}$$

$$= -\sum_k |g_k|^2 (2\overline{n_k}+1)\frac{1-\cos\omega_k t}{\omega_k^2}\mathcal{D}[\sigma_{11}]\rho_S$$
$$+ i\sum_k |g_k|^2 \Big\{\frac{\sin(\omega_k t)}{\omega_k^2} - \frac{t}{\omega_k}\Big\}\mathcal{L}[\sigma_{11}]\rho_S$$

$$\frac{\quad}{\omega_k^2} - \frac{\quad}{\omega_k} \Big] L[\sigma_{11}]\Big]$$

$$\rho_S(t) = \hat{T}\Big\{ \exp\Big[i \underbrace{\sum_k \left|\frac{g_k}{\hbar}\right|^2 \frac{t}{\omega_k}}_{\substack{=\Delta p t \\ \text{Polaron shift}}} L[\sigma_{11}] + \underbrace{\sum_k \left|\frac{g_k}{\hbar\omega_k}\right|^2 (2\bar{n}_k+1)(1-\cos\omega_k t)}_{=\gamma(t)} D[\sigma_{11}]$$

$$- i \underbrace{\sum_k \left|\frac{g_k}{\hbar\omega_k}\right|^2 \sin[\omega_k t]}_{\phi(t)} L[\sigma_{11}] \Big] \rho_S(0) \Big\}$$

$$= \exp\big[i\Delta p t\, L[\sigma_{11}] + \gamma(t,T)\, D[\sigma_{11}] - i\phi(t) L[\sigma_{11}] \big] \rho_S(0)$$

let's assume an initial coherence $\rho_S(0) = \sigma_{10}(0) = |1\rangle\langle 0|$

given $L[\sigma_{11}]\sigma_{10} = \sigma_{11}\sigma_{10} - \sigma_{10}\sigma_{11} = \sigma_{10}$

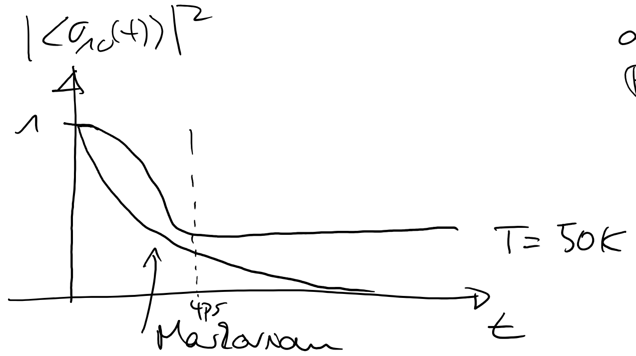
$$D[\sigma_{11}]\sigma_{10} = 2\underbrace{\sigma_{11}\sigma_{10}\sigma_{11}}_{=0} - \underbrace{\sigma_{11}\sigma_{10}}_{=\sigma_{10}} - \underbrace{\sigma_{10}\sigma_{11}}_{=0} = -\sigma_{10}$$

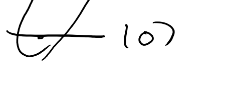
$$\rho_S^I(t) = \exp\big[i\Delta p t - \gamma(t,T) - i\phi(t) \big]\, \sigma_{10}(0) \qquad \langle 1|\sigma_{10}(0)$$

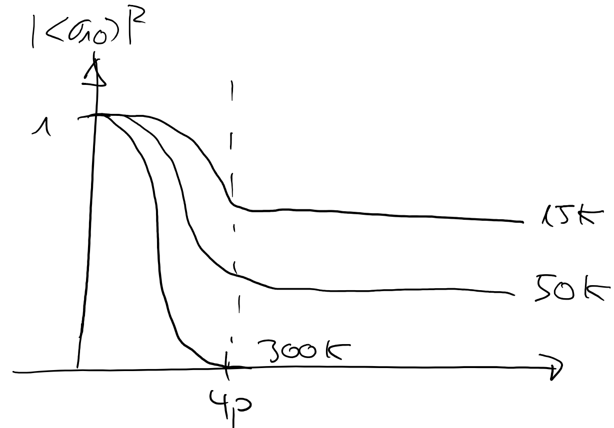
$$\langle 1|\rho_S(t)|0\rangle = \exp\Big[i(\omega_0+\Delta p)t - \sum_k \underbrace{\left|\frac{g_k}{\hbar\omega_k}\right|^2}_{\substack{\text{material} \\ \text{specific response}}} \Big[\underbrace{(2n_k+1)(1-\cos\omega_k t) + i\sin\omega_k t}_{\text{memory kernel}} \Big]\Big]$$

$$= \exp\Big[i(\omega_0+\Delta p)t - \sum_k \left|\frac{g_k}{\hbar\omega_k}\right|^2 \Big(2n_k+1 - n_k e^{i\omega_k t} - n_k e^{-i\omega_k t} + \tfrac{1}{2}e^{i\omega_k t}$$
$$- \tfrac{1}{2}e^{i\omega_k t} - \tfrac{1}{2}e^{-i\omega_k t} - \tfrac{1}{2}e^{-i\omega_k t}$$

$$= \exp\Big[i(\omega_0+\Delta p)t - \sum_k \left|\frac{g_k}{\hbar\omega_k}\right|^2 \Big(\underbrace{(n_k+1)(1-e^{-i\omega_k t})}_{\substack{\text{system loses coherence} \\ \text{even for } \bar{n}_k = 0 \\ \text{due to spontaneous} \\ \text{phonon emission}}} + n_k \underbrace{(1-e^{i\omega_k t})}_{\substack{\text{phonon} \\ \text{absorption}}} \Big)\Big] \langle\sigma_{10}\rangle$$

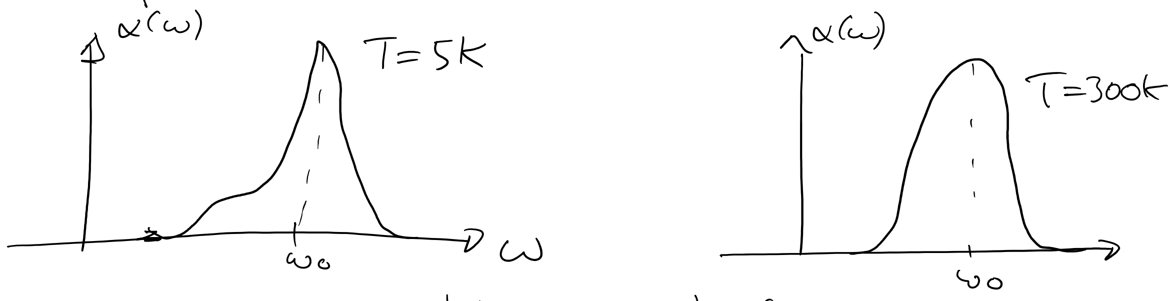






non-Markovian is very different from a

phenomenological model. after an initial applied coherence ($\frac{\pi}{2}$-pulse), not the whole coherence must get lost. it depends on the memory kernel and the temperature!!



asymmetries vanish for high temperatures if dephasing is mainly governed phonons.

$$\dot{\rho}_S^I = \exp\left\{ it\Delta L[\sigma_{11}] - i\phi(t) L[\sigma_{11}] + \gamma(t,T) D[\sigma_{11}] \right\}$$

$$\left[i\Delta L[\sigma_{11}] - i\dot{\phi}(t) L[\sigma_{11}] + \dot{\gamma}(t,T) D[\sigma_{11}] \right] \rho_S^I(0)$$

$$= i(\Delta - \dot{\phi}) [\sigma_{11}, \rho_S^I(t)] + \underbrace{\sum_q \frac{|g_q/\hbar|^2}{\omega_q^2} (2n_q+1) [-\sin\omega_q t]}_{=\dot{\gamma}(t,T)} D[\sigma_{11}] \rho_S^I(t)$$

is it trace conserving?

$$tr_S(\dot{\rho}_S^I) = i(\Delta - \dot{\phi}) \underbrace{tr_S\{ \sigma_{11}\rho_S^I(t) - \rho_S^I(t)\sigma_{11} \}}_{=\langle\sigma_{11}(t)\rangle - \langle\sigma_{11}(t)\rangle = 0}$$

$$+ \dot{\gamma}(t,T) \underbrace{tr_S\{ D[\sigma_{11}] \rho_S^I(t) \}}_{=0}$$

trace preserving – so model solved!!

$$\langle 1|\dot{\rho}_S^I|0\rangle = i(\Delta - \dot{\phi})\rho_{10} - i(\Delta - \dot{\phi}) \langle 1|\rho_S^I(t)\underbrace{\sigma_{11}|0\rangle}_{=0}$$

$= \dot{\rho}_{10}$

$$+ \dot{\gamma}\Big(2\langle 1|\sigma_{11}\rho_S^I(t)\underbrace{\sigma_{11}|0\rangle}_{=0} - \langle 1|\rho_S^I(t)\underbrace{\sigma_{11}|0\rangle}_{=0}$$

$$- \langle 1|\sigma_{11}\rho_S^I(t)|0\rangle \Big)$$

$$\dot{\rho}_{10} = [i\Delta - i\dot{\phi} - \dot{\gamma}]\rho_{10}$$

$$\Leftrightarrow \frac{\dot\rho_{10}}{\rho_{10}} = i\Delta - i\dot\phi - \dot\gamma$$

$$\ln \rho_{10}(t) - \ln \rho_{10}(0) = \int_0^t dt' \left[i\Delta - i\frac{d}{dt'}\phi(t') - \frac{d}{dt'}\gamma(t') \right]$$

$$= i\Delta t - i\phi(t) - \gamma(t,T)$$

$$\boxed{\rho_{10}(t) = e^{i\Delta t - i\phi(t) - \gamma(t,T)} \rho_{10}(0)}$$

we reproduced within a non-Markovian master equation approach, the independent boson model.