qu. master equ:

$$\frac{\partial}{\partial t}\hat{\rho} = -\frac{i}{\hbar}[\hat{\mathcal{H}}_s, \hat{\rho}] + \sum_{\gamma > 1}\left[\hat{L}_\gamma \rho \hat{L}_\gamma^+ - \frac{1}{2}\hat{L}_\gamma^+ \hat{L}_\gamma \hat{\rho} - \frac{1}{2}\hat{\rho}\hat{L}_\gamma^+ \hat{L}_\gamma\right]$$

$$\hat{L}_\gamma = \sqrt{a_\gamma}\,\hat{\Lambda}_\gamma$$

$$\hat{\Lambda}_\gamma = \begin{cases} |i\rangle\langle j| & i \neq j \quad \text{jump oper.} \\ \frac{\hat{I} - 2|i\rangle\langle i|}{\sqrt{N}} & \text{dephasing oper.} \quad i = 2, \ldots, N \end{cases}$$

N = dim. of Hilbert space

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example: spin $\frac{1}{2}$ particle interacting w/ env.

$N = 2$ $\quad |\uparrow\rangle = |1\rangle$

$\quad |\downarrow\rangle = |2\rangle$

$N^2 - 1 = 3$ Lindblad oper. $\hat{\Lambda}_\gamma$

$$\hat{\Lambda}_1 = |1\rangle\langle 2| = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$ in $\{|1\rangle, |2\rangle\}$ basis

$$\hat{\Lambda}_2 = |2\rangle\langle 1| = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$\hat{\Lambda}_3 = \frac{1}{\sqrt{2}}(\hat{I} - 2|2\rangle\langle 2|) = \frac{1}{\sqrt{2}}\left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - 2\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}\right]$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$tr(\hat{\Lambda}_\gamma) = 0$

$tr(\hat{\Lambda}_\gamma \hat{L}_\delta) = \delta_{\gamma\delta}$

coeff's: $a_1 = W_{12}$ $\qquad a_2 = W_{21}$ $\qquad a_3 = \Gamma_2$

$$\hat{L}_1 = \sqrt{W_{12}}\,\hat{\Lambda}_1 \qquad \hat{L}_2 = \sqrt{W_{21}}\,\hat{\Lambda}_2 \qquad \hat{L}_3 = \sqrt{\Gamma_2}\,\hat{\Lambda}_3$$

assume $\hat{\mathcal{H}}_s$ is diagonal in $\{ |1\rangle, |2\rangle \}$

$$\hat{\mathcal{H}}_s = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

plug this all into Lindblad eq. + take $\langle i | \sim | i \rangle$ sandwich:

$$\langle i | \frac{\partial \hat{\rho}}{\partial t} | i \rangle = \langle i | \text{RHS} | i \rangle \qquad i = 1, 2$$

conserv. of prob. equation (like class. mast. eqn.)

algebra:
$$\frac{\partial \rho_{ii}}{\partial t} = \sum_{j=1}^{2} \Big(\underbrace{\underset{\text{prob. to jump } |j\rangle \to |i\rangle}{W_{ij}} \; \underset{\text{prob. of } |j\rangle}{\rho_{jj}}}_{\text{gain of prob. of state } |i\rangle} - \underbrace{\underset{\text{prob. to jump } |i\rangle \to |j\rangle}{W_{ji}} \; \underset{\text{prob. of } |i\rangle}{\rho_{ii}}}_{\text{loss of prob. of } |i\rangle} \Big)$$

ρ_{ii} = "population"

$\sum_i \rho_{ii} = 1 \qquad \rho_{ii} \geq 0$

$\rho_{ii} \sim$ "classical prob": prob. to measure $|i\rangle$ in ensemble

$N = 2$:
$$\frac{\partial}{\partial t} \rho_{11} = - W_{21} \rho_{11} + W_{12} \rho_{22}$$
$$\frac{\partial}{\partial t} \rho_{22} = + W_{21} \rho_{11} - W_{12} \rho_{22}$$

solution: $i=1,2$

$$\rho_{ii}(t) = \rho_{ii}^{s} + \left(\rho_{ii}(0) - \rho_{ii}^{s}\right) e^{-t/T_1}$$

$$1 \underset{W_{12}}{\overset{W_{21}}{\rightleftarrows}} 2$$

$$\rho_{11}^{s} = \frac{W_{12}}{W_{12}+W_{21}} \qquad \rho_{22}^{s} = \frac{W_{21}}{W_{12}+W_{21}}$$

stat. state sol'ns for ρ_{ii}

$$T_1 = \frac{1}{W_{12}+W_{21}} > 0$$

relaxation time to reach stat. state

$$\rho_{ii}(0) = \rho_{ii}(0) \qquad \rho_{ii}(t\to\infty) = \rho_{ii}^{s}$$

$i \neq j$: $\langle i | \frac{\partial \hat{\rho}}{\partial t} | j \rangle = \langle i | \text{RHS} | j \rangle$

algebra: $$\frac{\partial \rho_{ij}}{\partial t} = \left(-i\omega_{ij} - \gamma_{ij}\right)\rho_{ij}$$

$$\omega_{ij} = \frac{E_i - E_j}{\hbar} \qquad \gamma_{ij} = \frac{1}{2}\sum_k \left(W_{kj} + W_{ki}\right) + 2\left(\Gamma_i + \Gamma_j\right) \geq 0$$

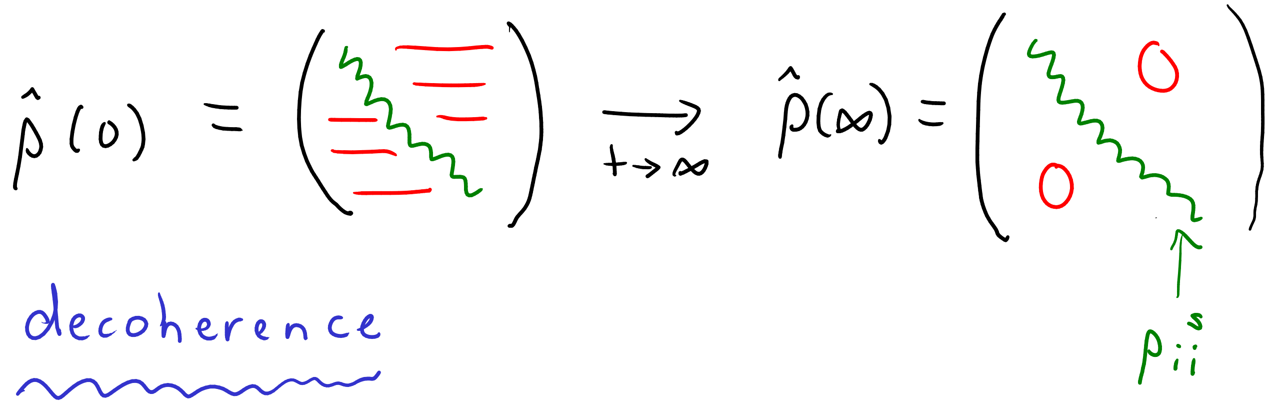
$$\rho_{ij}(t) = e^{-i\omega_{ij}t}\, e^{-\gamma_{ij}t}\, \rho_{ij}(0)$$

no environ: $W_{ij}, \Gamma_i = 0 \Rightarrow \gamma_{ij} = 0$

$$\rho_{ij}(t) = e^{-i\omega_{ij}t}\rho_{ij}(0)$$

off-diag elem change phase, but persist

environ: $\gamma_{ij} > 0 \Rightarrow \rho_{ij}(t) \to 0$ as $t \to \infty$



decoherence

T_1 = time scale of equilibration

$$\rho_{ii}(t) \to \rho_{ii}^s$$

$T_2 = \dfrac{1}{\gamma_{12}}$ = time scale for off-diag. elements to vanish (decoh. time)

for H^+ in a protein: $T_1 \approx 250$ ms

$T_2 \approx 0.1 - 1$ ms

missing links:

1) we have not proven LDB in quantum context

if LDB is true: $\dfrac{W_{12}}{W_{21}} = e^{-\beta(E_1 - E_2)}$, $\beta = \dfrac{1}{k_B T}$

$$\left.\begin{aligned} \rho_{11}^s &= \frac{W_{12}}{W_{12} + W_{21}} = \frac{e^{-\beta E_1}}{Z} \\ \rho_{22}^s &= \frac{W_{21}}{W_{12} + W_{21}} = e^{-\beta E_2}/Z \end{aligned}\right\} \text{Boltz. equil.}$$

classical chaos $\Rightarrow$ ergodicity + mixing $\Rightarrow$ LDB + Boltzmann

quantum chaos $\not\Rightarrow$ quantum LDB + Boltzmann

2) there is no quantum operator for "work":

how to define work in quantum thermodynamics?