Rovnováha v sekulární Redfieldově teorii

$$\frac{\partial}{\partial t}\rho(t) = -\frac{i}{\hbar}[H_S,\rho] - R(t)\rho(t)$$

Jak bude vypadat stav pro $t \to \infty$? Jaká bude rovnováha systému?

Sekulární tensor: koherence

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}(t) = -i\omega_{\alpha\beta}\rho_{\alpha\beta}(t) - R_{\alpha\beta\alpha\beta}(t)\,\rho_{\alpha\beta}(t)$$

$$R_{\alpha\beta\alpha\beta}(t) \equiv R_{\alpha\beta\alpha\beta} = \gamma$$

$\Rightarrow$ řešení je

$$\rho_{\alpha\beta}(t) = \rho_{\alpha\beta}(0)\, e^{-i\omega_{\alpha\beta}t - \gamma t}$$

$t \to \infty$ $\qquad \rho_{\alpha\beta}(t) \to 0$

V rovnováze nejsou žádné koherence.

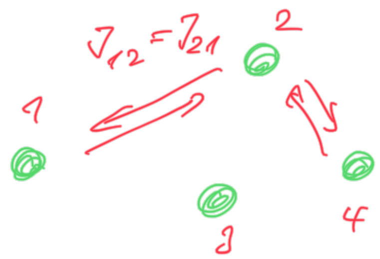
Sekulární tensor: populace

$$\frac{\partial}{\partial t}\rho_{\alpha\alpha}(t) = \sum_{\beta} K_{\alpha\beta}\,\rho_{\beta\beta}(t)$$

V rovnováze platí: $\quad \frac{\partial}{\partial t}\rho_{\alpha\alpha}(t) = 0$

$$\Rightarrow \quad \boxed{\sum_{\beta} K_{\alpha\beta}\,\rho_{\beta\beta} = 0}$$

V rovnováze tedy platí, že každé dva „proudy" $J_{\alpha\beta}$ a $J_{\beta\alpha}$ se rovnají



„Proud" $\Rightarrow$ $J_{\alpha\beta} = K_{\alpha\beta}\rho_{\beta\beta}$

detailní rovnováha

$$\Rightarrow \quad \boxed{K_{\alpha\beta}\rho_{\beta\beta} = K_{\beta\alpha}\rho_{\alpha\alpha}}$$

$$\rho_{\beta\beta} = \frac{K_{\beta\alpha}}{K_{\alpha\beta}}\rho_{\alpha\alpha}$$

Použijeme to:

$$\Rightarrow \sum_\beta \cancel{K_{\alpha\beta}}\frac{K_{\beta\alpha}}{\cancel{K_{\alpha\beta}}}\rho_{\alpha\alpha} = \underbrace{\Big(\sum_\beta K_{\beta\alpha}\Big)}_{=0}\rho_{\alpha\alpha} = 0$$

sledujme vztah mezi rychlostními konstantami $K_{\alpha\beta}$ a $K_{\beta\alpha}$

$$K_{\alpha\beta} = \frac{1}{\hbar^2}\sum_n |\langle\alpha|n\rangle|^2|\langle\beta|n\rangle|^2\tilde{C}_n(\omega_{\beta\alpha})$$

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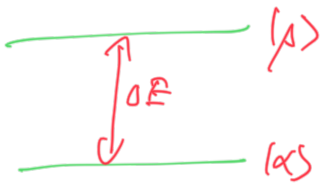
Víme:

$$\tilde{C}_n(\omega_{\beta\alpha}) = \xi\,\tilde{C}_n(\omega_{\alpha\beta}) \Rightarrow \boxed{K_{\alpha\beta} = \xi K_{\beta\alpha}}$$

$$\Rightarrow \rho_{\beta\beta} = \frac{1}{\xi}\rho_{\alpha\alpha}$$

Známe univerzální pravidlo:

$$\rho_{\beta\beta} = e^{-\frac{\Delta E}{k_BT}}\rho_{\alpha\alpha} \qquad \Delta E = \varepsilon_\beta - \varepsilon_\alpha$$



$$\Rightarrow \boxed{\tilde{C}_m(\omega_{\beta\alpha}) = e^{+\frac{\hbar\omega_{\beta\alpha}}{k_B T}}\, \tilde{C}_m(\omega_{\alpha\beta})}$$

$$\tilde{C}_m(\omega) \sim \tilde{C}_m(-\omega)$$

Korelační funkce lázně

$$C_m(t) = tr_B\{\Delta V_m(t)\,\Delta V_m\, w_{eq}\}$$

$$\tilde{C}_m(\omega) = \int_{-\infty}^{\infty} dt\; C_m(t)\, e^{i\omega t}$$

Vyjádříme stopu v nějaké bázi $\{|\nu\rangle\}$ ← vlastní stavy H_B ; $H_B|\nu\rangle = \mathcal{E}_\nu|\nu\rangle$

$$C_m(t) = \sum_\nu \langle\nu|\, U_B^\dagger(t)\,\Delta V_m\, U_B(t)\,\Delta V_m\, w_{eq}\,|\nu\rangle$$

$\to P(\nu) \approx e^{-\frac{\mathcal{E}_\nu}{k_B T}}$

$$U_B(t) = \sum_\nu e^{-i\frac{\mathcal{E}_\nu}{\hbar}t}\,|\nu\rangle\langle\nu| \quad ; \quad w_{eq} = \sum_\nu P(\nu)\,|\nu\rangle\langle\nu|$$

Jak vypadá ΔV_m ?

$$\langle\nu|\Delta V|\mu\rangle = U_{\nu\mu}$$

$$C_m(t) = \sum_{\nu\mu} e^{i\frac{\mathcal{E}_\nu}{\hbar}t}\, U_{\nu\mu}\, e^{-i\frac{\mathcal{E}_\mu}{\hbar}t}\, U_{\mu\nu}\, P(\nu)$$

$$= \sum_{\nu\mu} |U_{\nu\mu}|^2\, e^{i\omega_{\nu\mu}t}\, P(\nu)$$

$$\tilde{C}_m(\omega) = \sum_{\nu\mu} |U_{\nu\mu}|^2\, P(\nu) \int_{-\infty}^{\infty} dt\; e^{i(\omega_{\nu\mu}+\omega)t}$$

$$= \sum_{\nu\mu} |U_{\nu\mu}|^2\, P(\nu)\; 2\pi\, \delta(\omega_{\mu\nu} - \omega)$$

ukážeme vyjádření $\tilde{C}_\mu(-\omega)$

$$\tilde{C}_\mu(-\omega) = \sum_{\mu\nu} 2\pi |V_{\nu\mu}|^2 P(\nu)\,\delta(\omega_{\mu\nu}+\omega)$$

$$= \sum_{\mu\nu} 2\pi |V_{\nu\mu}|^2 P(\nu)\,\delta(-(\omega_{\nu\mu}-\omega))$$

$$= \sum_{\mu\nu} 2\pi |V_{\nu\mu}|^2 P(\nu)\,\delta(\omega_{\nu\mu}-\omega)\cdot\frac{P(\mu)}{P(\mu)}$$

$$\frac{P(\nu)}{P(\mu)} = e^{-\frac{\omega_{\nu\mu}}{k_BT}} = e^{-\frac{\omega}{k_BT}}$$

$$= \sum_{\mu\nu} 2\pi |V_{\nu\mu}|^2 P(\mu)\,\delta(\omega_{\nu\mu}-\omega)\cdot e^{-\frac{\omega}{k_BT}}$$

Prohodíme jména indexů $\mu\to\nu$, $\nu\to\mu$

$$= \underbrace{\sum_{\mu\nu} 2\pi |V_{\nu\mu}|^2 P(\nu)\,\delta(\omega_{\mu\nu}-\omega)}_{\tilde{C}_\mu(\omega)}\, e^{-\frac{\omega}{k_BT}}$$

$$\boxed{\tilde{C}_\mu(-\omega) = \tilde{C}_\mu(\omega)\, e^{-\frac{\omega}{k_BT}}}$$

$$\Downarrow$$

$$\boxed{K_{\alpha\beta} = e^{-\frac{\omega_{\alpha\beta}}{k_BT}} K_{\beta\alpha}}$$

1) 

$-\frac{\omega_{\beta\alpha}}{k_BT}$

$K_{\beta\alpha} = e \quad K_{\alpha\beta}$

V Redfieldových rovnicích platí kanonická detailní rovnováha