Sekulární Redfieldovy rovnice

Nyní stačí uvažovat elementy

$$\left.\begin{array}{l} R_{\alpha\beta\alpha\beta} \\ R_{\alpha\alpha\beta\beta} \end{array}\right\} \alpha \neq \beta$$

$$R_{\alpha\alpha\alpha\alpha}$$

4 členy

I. $\quad - H_t H_\tau \rho$

II. $\quad + H_t \rho H_\tau$

III. $\quad + H_\tau \rho H_t$

IV. $\quad - \rho H_\tau H_t$

I. = IV.$^+$

II. = III.$^+$

Stačí vyčíslit členy I. a II.

Člen I.

$$\frac{\partial}{\partial t}\rho_{\alpha\beta} : \qquad H_{t\,\alpha\gamma} H_{\tau\,\gamma\delta} \rho_{\delta\beta} \xrightarrow{\text{sekulární ap.}} \delta = \alpha$$

$$\Rightarrow \left(\sum_\gamma H_{\alpha\gamma} H_{\gamma\alpha}\right) \rho_{\alpha\beta}$$

$$\frac{\partial}{\partial t}\rho_{\alpha\alpha} : \qquad H_{t\,\alpha\gamma} H_{\tau\,\gamma\delta} \rho_{\delta\alpha} \xrightarrow{\text{s.a.}} \delta = \alpha$$

$$\Rightarrow \left(\sum_\gamma H_{\alpha\gamma} H_{\gamma\alpha}\right) \rho_{\alpha\alpha}$$

Člen II.

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}: \qquad H_{\alpha\gamma}\rho_{\gamma\delta}H_{\delta\beta} \xrightarrow{\text{s.a.}} \begin{matrix}\gamma=\alpha\\ \delta=\beta\end{matrix}$$

$$\Rightarrow H_{\alpha\alpha}\rho_{\alpha\beta}H_{\beta\beta}$$

$$\frac{\partial}{\partial t}\rho_{\alpha\alpha}: \qquad H_{\alpha\gamma}\rho_{\gamma\delta}H_{\delta\alpha} \xrightarrow{\text{s.a.}} \begin{matrix}\gamma=\beta\\ \delta=\beta\end{matrix}$$

$$\Rightarrow H_{\alpha\beta}\rho_{\beta\beta}H_{\beta\alpha}$$

v detailu – členy I. a II.

$$H_I = \sum_n \Delta V_n |n\rangle\langle n|$$

Člen I.

$$\frac{1}{\hbar^2}\mathrm{tr}_B\{w_{eq}H_I H_I(-\tau)\}\rho(t)$$

$$= \sum_n \frac{1}{\hbar^2}\underbrace{\mathrm{tr}_B\{w_{eq}\,\Delta V_n\,\Delta V_n(-\tau)\}}_{\mathrm{tr}_B\{\Delta V_n(\tau)\Delta V_n w_{eq}\}} K_n K_n(-\tau)\rho(t)$$

$U_B(\tau)$ $\quad U_B^\dagger(\tau)$

$K_n = |n\rangle\langle n|$

$U_S(\tau)$ $\quad U_S^\dagger(\tau)$

$$= \langle\alpha|\sum_n \frac{1}{\hbar^2}\underbrace{\mathrm{tr}_B\{\Delta V_n(\tau)\Delta V_n w_{eq}\}} K_n K_n(-\tau)\rho(t)|\beta\rangle$$

$$= \sum_n\sum_{\gamma\delta}\frac{1}{\hbar^2}C_n(\tau)\langle\alpha|n\rangle\langle n|\gamma\rangle e^{-i\frac{\varepsilon_\gamma}{\hbar}\tau}\langle\gamma|n\rangle\langle n|\delta\rangle e^{+i\omega_\delta\tau}\rho_{\delta\beta}(t)$$

$\frac{\varepsilon_\gamma}{\hbar} \equiv \omega_\gamma$

Koherence $\longrightarrow$ $\delta\equiv\alpha$

$$\sum_{n\gamma}\frac{1}{\hbar^2}C_n(\tau)\,|\langle\alpha|n\rangle|^2\,|\langle\gamma|n\rangle|^2 e^{-i\omega_{\gamma\delta}\tau}\rho_{\alpha\beta}(t)$$

$$\Uparrow$$

$$R^{(I)}_{\alpha\beta\alpha\beta}(t)$$

$$R^{(I)}_{\alpha\alpha\alpha\alpha}(t) \equiv R^{(I)}_{\alpha\beta\alpha\beta}(t)$$

Člen II.

$$\frac{1}{\hbar^2} tr_B \{ H_I(-\tau) w_{eq} \rho(t) H_I \}$$

$$= \frac{1}{\hbar^2} \sum_n tr_B \{ \Delta V_n(-\tau) w_{eq} \Delta V_n \} K_n(-\tau) \rho(t) K_n$$

$$= \langle\alpha| \frac{1}{\hbar^2} \sum_n tr_B \{ \Delta V_n(\tau) \Delta V_n w_{eq} \} K_n(-\tau) \rho(t) K_n |\beta\rangle$$

$$= \frac{1}{\hbar^2} \sum_n C_n(\tau) \sum_{\gamma\delta} \langle\alpha|n\rangle\langle n|\gamma\rangle e^{-i\omega_{\alpha\gamma}\tau} \rho_{\gamma\delta}(t) \langle\delta|n\rangle\langle n|\beta\rangle$$

$$= \frac{1}{\hbar^2} \sum_{\gamma\delta} \sum_n C_n(\tau) \langle\alpha|n\rangle\langle n|\gamma\rangle\langle\delta|n\rangle\langle n|\beta\rangle \times e^{-i\omega_{\alpha\gamma}\tau} \rho_{\gamma\delta}(t)$$

Koherence $\gamma = \alpha$
$\delta =$

$$\frac{1}{\hbar^2} \sum_n C_n(\tau) |\langle\alpha|n\rangle|^2 |\langle\beta|n\rangle|^2 \rho_{\alpha\beta}(t$$

Populace $\beta = \alpha$
$\delta = \gamma = \beta$

$$\frac{1}{\hbar^2} \sum_\beta \sum_n C_n(\tau) |\langle\alpha|n\rangle|^2 |\langle n|\beta\rangle|^2 e^{-i\omega_{\alpha\beta}\tau} \rho_{\beta\beta}(t)$$

Celkově:

$$R^{(II)}_{\alpha\beta\alpha\beta}(t) = \frac{1}{\hbar^2}\int_0 d\tau \sum_n C_n(\tau)\, |\langle\alpha|n\rangle|^2 |\langle\beta|n\rangle|^2$$

$$R^{(II)}_{\alpha\alpha\beta\beta}(t) = \frac{1}{\hbar^2}\int_0^t d\tau \sum_n C_n(\tau)\, e^{-i\omega_{\alpha\beta}\tau} |\langle\alpha|n\rangle|^2 |\langle\beta|n\rangle|^2$$

členy III. a IV.

máme

$$R^{(III)}_{\alpha\beta\gamma\delta} = \left(R^{II}_{\beta\alpha\delta\gamma}\right)^* ; \quad R^{IV}_{\alpha\beta\gamma\delta} = \left(R^{(I)}_{\beta\alpha\delta\gamma}\right)^*$$

tedy: $\beta \neq \alpha$

$$\boxed{R_{\alpha\alpha\beta\beta}(t)} = R^{(II)}_{\alpha\alpha\beta\beta}(t) + \left(R^{(II)}_{\alpha\alpha\beta\beta}(t)\right)^* =$$

$$\boxed{= 2\,\mathrm{Re}\, R^{(II)}_{\alpha\alpha\beta\beta}(t)}$$

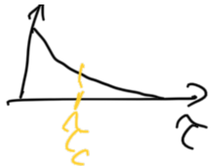
$$\boxed{R_{\alpha\alpha\alpha\alpha}(t) = 2\,\mathrm{Re}\, R^{(II)}_{\alpha\alpha\alpha\alpha}(t) + 2\,\mathrm{Re}\, R^{(I)}_{\alpha\alpha\alpha\alpha}(t)}$$

$$\boxed{\begin{aligned} R_{\alpha\beta\alpha\beta}(t) = {} & R^{(II)}_{\alpha\beta\alpha\beta}(t) + \left(R^{(II)}_{\beta\alpha\beta\alpha}(t)\right)^* \\ & + R^{(I)}_{\alpha\beta\alpha\beta}(t) + \left(R^{(I)}_{\beta\alpha\beta\alpha}(t)\right)^* \end{aligned}}$$

Rychlostní konstanty přenosu populací

$$\boxed{K_{\alpha\beta}(t) = -R_{\alpha\alpha\beta\beta}(t)} = -2\,\mathrm{Re}\, R^{(II)}_{\alpha\alpha\beta\beta}(t)$$

$$\boxed{= \frac{2}{\hbar^2}\,\mathrm{Re}\int_0^t d\tau \sum_n C_n(\tau)\, |\langle\alpha|n\rangle|^2 |\langle\beta|n\rangle|^2 e^{-i\omega_{\alpha\beta}t}}$$

$C_n(\tau) =$ 

$$\lim_{\substack{t\to\infty \\ t > \tau_c}} \Rightarrow \quad K_{\alpha\beta} \equiv K_{\alpha\beta}(t \to \infty)$$

$$2\,\mathrm{Re}\int_0^\infty d\tau\, C_n(\tau)\, e^{-i\omega_{\alpha\beta} t} = \int_0^\infty d\tau\, C_n(\tau)\, e^{-i\omega_{\alpha\beta}\tau} + \int_0^\infty d\tau\, C_n^*(\tau)\, e^{i\omega_{\alpha\beta}\tau}$$

$$\tau' = -\tau$$

$$= \int_0^\infty d\tau\, C_n(\tau)\, e^{-i\omega_{\alpha\beta}\tau} + \int_{-\infty}^{0} d\tau\, C_n^*(-\tau)\, e^{-i\omega_{\alpha\beta}\tau} \qquad C_n(-\tau) = C_n^*(\tau)$$

$$= \int_{-\infty}^{\infty} d\tau\, C_n(\tau)\, e^{-i\omega_{\alpha\beta}\tau} = FT\left[C_n(\tau)\right](\omega_{\beta\alpha})$$

$$= \tilde{C}_n(\omega_{\beta\alpha})$$

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

$$\alpha \neq \beta$$

FT korelační fce

~ spektrální hustota

$$\overline{K}_{\alpha\alpha} = \frac{1}{\hbar^2}\sum_n |\langle\alpha|n\rangle|^4\, \tilde{C}_n(0) \quad \leftarrow$$ co tohle znamená?