Försterova teorie přenosu

Teorie přenosu energie mezi slabě vázanými molekulami

– resonanční vazba je parametrem poruchové teorie

V předcházejících jsme odvodili:

$$\frac{\partial}{\partial t} P_a(t) = -\sum_b K_{ba}(t)\, P_a(t) + \sum_b K_{ab}(t)\, P_b(t),$$

kde

$$K_{ab}(t) = \frac{2\,|J_{ab}|^2}{\hbar^2} \mathrm{Re} \int_0^t d\tau\, \mathrm{tr}_B \left\{ U_b^\dagger(\tau) U_a(\tau) W_{eq}^b \right\}$$

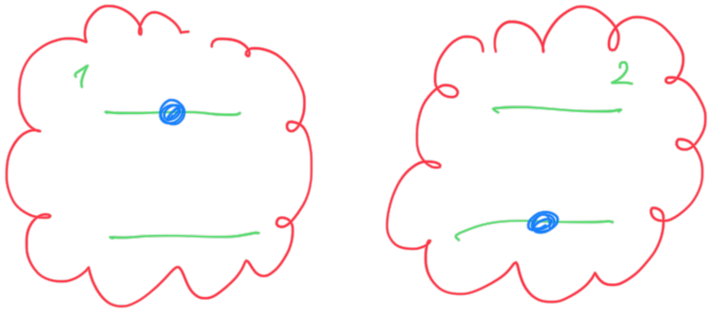
Försterova teorie – pozoruhodná vlastnost

rychlostní konstanta se dá vyjádřit přímo pomocí měřitelných veličin.

Dokažme to:

Zkoumejme člen pod integrálem:

$$\mathrm{tr}_B \left\{ U_b^\dagger(\tau) U_a(\tau) W_{eq}^b \right\}$$



stav $|b\rangle$

1… excitovaná

2… základní stav

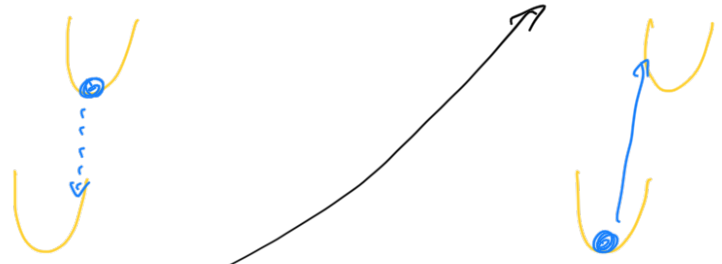
$$\hat{w}^{b}_{eq} = \hat{w}^{1e}_{eq}\,\hat{w}^{2g}_{eq} \;;\quad \hat{U}_a(\tau) = \hat{U}_1^{g}(\tau)\,\hat{U}_2^{e}(\tau)$$

$$\hat{U}_b(\tau) = \hat{U}_1^{e}(\tau)\,\hat{U}_2^{g}(\tau)$$

$$\sim e^{\frac{i}{\hbar}\varepsilon_e\tau}\, e^{-\frac{i}{\hbar}\varepsilon_g\tau} \leftarrow \omega_{eg} = \frac{\varepsilon_e-\varepsilon_g}{\hbar}$$

$$tr_B\{\dots\} = tr_B^{1}\{U_e^{\dagger}(\tau)U_g(\tau)w_{eq}^{e}\}\, tr_B^{2}\{U_g^{\dagger}(\tau)U_e(\tau)w_{eq}^{g}\}$$

$$= e^{i\omega_{eg}\tau}\, tr_B^{1}\{\tilde{U}_e^{\dagger}(\tau)\tilde{U}_g(\tau)w_{eq}^{e}\}\, e^{-i\omega_{eg}\tau}\, \underbrace{tr_B^{2}\{\tilde{U}_g^{\dagger}(\tau)\tilde{U}_e(\tau)w_{eq}^{g}\}}$$



$$e^{-i\omega_{eg}\tau}\, tr_B^{2}\{\tilde{U}_g^{\dagger}(\tau)\tilde{U}_e(\tau)w_{eq}^{g}\} = e^{-i\omega_{eg}\tau}\, tr_B^{2}\{\tilde{U}_e(\tau)\,w_{eq}^{g}\,\tilde{U}_g^{\dagger}(\tau)\}$$

$$\simeq \rho_{eg}(\tau)$$

máme video na téma rozfázování koherence

$$\rho_{eg}(\tau) = e^{-i\omega_{eg}\tau}\, e^{-g(\tau)} = G_A(t)$$

tzv. lineshape funkce

$$g(t) = \int_0^t d\tau \int_0^{\tau} d\tau' C(\tau') \leftarrow \text{korelační funkce lázně}$$

$$\alpha(\omega) \approx \int_{-\infty}^{\infty} dt\, e^{-i\omega_{eg}t - g(t) + i\omega t} \equiv \tilde{G}(\omega - \omega_{eg})$$

<u>Vlastnosti:</u>

$$g(-t) = g^*(t)$$

$$g(-t) = \int_0^{-t} d\tau \int_0^{\tau} d\tau' C(\tau') = -\int_0^{t} d\tau'' \int_0^{-\tau''} d\tau' C(\tau') = \int_0^{t} d\tau'' \int_0^{\tau''} d\tau''' C(-\tau''')$$

$$= \int_0^t d\tau \int_0^{\tau} d\tau' C^*(\tau') = g^*(t)$$

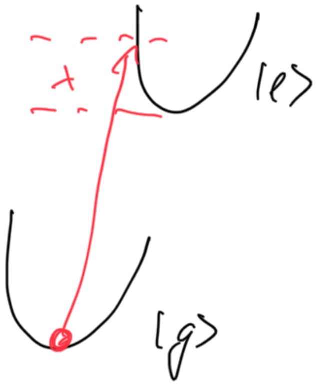
$$\tilde{G}(\omega) = \int_0^{\infty} dt\, e^{-g(t) + i\omega t} + \int_{-\infty}^{0} dt \ldots = \int_0^{\infty} dt\, e^{-i\omega t - g(t)} + \int_0^{\infty} dt\, e^{i\omega t - g^*(t)}$$

$$= 2\,\mathrm{Re} \int_0^{\infty} dt\, e^{-g(t) + i\omega t} = \ldots \text{ reálný line shape}$$

$$\int_{-\infty}^{\infty} d\omega\, \tilde{G}(\omega) = 2\pi\, FT^{-1}\left[\tilde{G}(\omega)\right](0) = 2\pi\, e^{-i\omega_0 \cdot 0 - \overbrace{g(0)}^{=0}} = 2\pi$$

normalizované na 2π

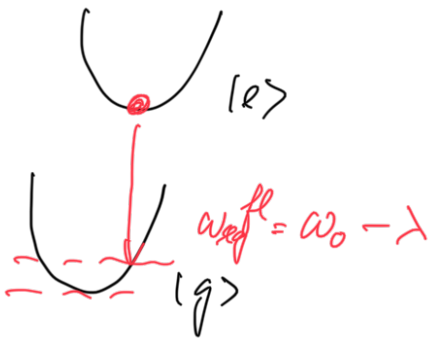
Jedna část výrazu odpovídá tvaru absorpční čáry. Popisuje pozice:



$$\omega_{eg}^{abs} = \omega_0 + \lambda$$

$$\left(\text{nebo } \frac{\lambda}{\hbar}\right)$$

Druhý výraz: emise – fluorescence



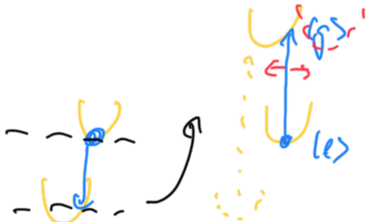
$$\Rightarrow \boxed{\omega_{eg}^{fl} = \omega_{eg}^{ab} - 2\lambda}$$

minulý výraz

$$G_A(t) = e^{-g(t) - i\omega_{eg}^{ab} t} \to \tilde{G}_A(\omega - \omega_0 - \lambda) = \tilde{G}_A(\omega - \omega_{eg}^{ab})$$

Bychom měli mít

$$G_D(t) = e^{i\omega_{eg} t}\, \mathrm{tr}_B\left\{ U_e^{\dagger}(\tau) U_g(\tau) W_{eq}^{e} \right\}$$



$$\Delta\hat{V} \approx \pm d\hat{q}$$

$$\Delta\hat{V}\Delta\hat{V} \to |d|^2$$

$$G_A(t) = e^{-g_A(t) - i\omega_A t} \xrightarrow{FT} \tilde{G}_A(\omega - \omega_A)$$

$$G_D(t) = e^{-g_D(t) + i(\omega_D - 2\lambda)t} \xrightarrow{FT} \tilde{G}_D(\omega + \omega_D - 2\lambda)$$

Vraťme se ke relaxační konstantě v $t \to \infty$

$$K_{AD}(\infty) = \frac{|J_{ab}|^2}{\hbar^2} 2\mathrm{Re} \int_0^\infty d\tau\, G_D(\tau) G_A(\tau)$$

Zkusme zformulovat rychlostní konstantu pomocí spektr. čar.

$$G_A(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \tilde{G}_A(\omega-\omega_A)\, e^{-i\omega\tau}$$

$$G_D(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega'\, \tilde{G}_D(\omega'+\omega_D-2\lambda)\, e^{-i\omega'\tau}$$

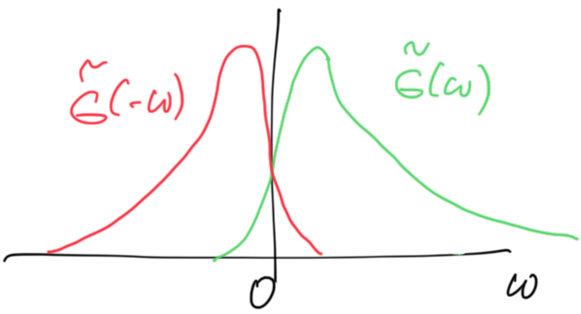
$$\Rightarrow K_{AD} = \frac{|J_{as}|^2}{\hbar^2}\underline{\int_{-\infty}^{\infty} d\tau}\, \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega'\, \tilde{G}_A(\omega-\omega_A)\tilde{G}_D(\omega'+\omega_D-2\lambda) \underbrace{\times e^{-i\omega\tau-i\omega'\tau}}_{2\pi\delta(\omega+\omega')}$$

$$= \frac{|J_{as}|^2}{\hbar^2}\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \tilde{G}_A(\omega-\omega_A)\tilde{G}_D(-\omega+\omega_D-2\lambda)$$

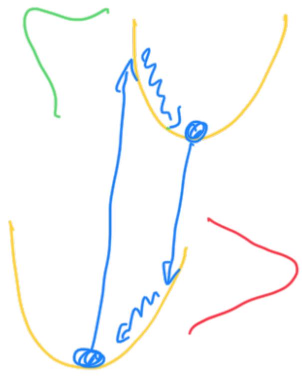
$$= \frac{|J_{as}|^2}{\hbar^2}\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \tilde{G}_A(\omega-\omega_A)\tilde{G}_D(-(\omega-(\omega_D-2\lambda)))$$

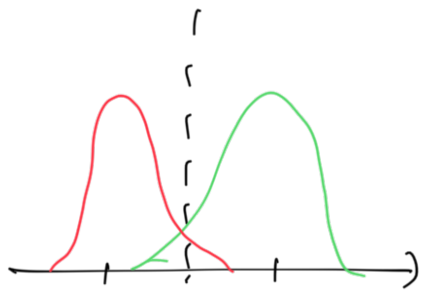
sedí na fluorescenční frekvenci

Co je $\tilde{G}_D(-\omega)$ ← zrcadlově odrážený tvar čáry



Relaxační konstanta vypadá jako překryv absorpčního spektra akceptoru A s fluorescenčním spektrem donoru D.





$$\omega = 2\pi\nu$$

$$\Rightarrow K_{AD} = \frac{|J_{as}|^2}{\hbar^2}\int_{-\infty}^{\infty} d\nu\, \bar{G}_A(\nu-\nu_A)\,\bar{G}_F(-(\nu-(\nu_D-2\lambda)))$$

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, G(\omega) = \frac{1}{\cancel{2\pi}}\int_{-\infty}^{\infty} d\nu\, \cancel{2\pi}\, G(2\pi\nu) = \int_{-\infty}^{\infty} d\nu\, \bar{G}(\nu) = 1$$

Skutečná spektra mají jiné závislosti na ν:

<u>absorpce</u>: $\alpha(\nu) \simeq \nu\, \bar{G}_A(\nu)$

<u>Fluorescence</u>: $f(\nu) \simeq \nu^3\, \bar{G}_F(\nu)$

$$\bar{G}_A(\nu) = \frac{1}{N_A}\frac{\alpha(\nu)}{\nu}\ ; \quad \bar{G}_F(\nu) = \frac{1}{N_f}\frac{f(\nu)}{\nu^3} \qquad \frac{1}{N_f} f(\nu) =: \bar{f}(\nu)$$

$$\boxed{K_{AD} = \frac{|J_{as}|^2}{\hbar^2}\int_{-\infty}^{\infty} d\nu\, \frac{1}{\nu^4}\,\bar{\alpha}(\nu)\,\bar{f}(\nu)}$$

Závislost J_{as} na vzdálenosti

$$J_{as} \sim \frac{1}{r^3}$$ ← dipól-dipólová interakce

$$K_{AD} = \beta_{as} \frac{1}{r^6} \int \frac{\bar{\alpha}(\nu)\,\bar{f}(\nu)}{\nu^4}\, d\nu$$