Lecture 5: Excitation Energy Transfer.

* Exciton Hamiltonian.
* Driving force for energy transfer & electron transfer
* Redfield theory
* Population dynamics & detailed balance.

In the last lecture we discussed properties of time-correlation functions. You will soon see that they are useful. This lecture, finally, we approach real physical problems ⇒ what we set out to do is dissipative dynamics, with focus on ET & EET, in molecular systems.

* Energy relaxation in molecular systems

* single chromophore : Vibrational relaxation / Internal conversion / Intersystem crossing . . . .

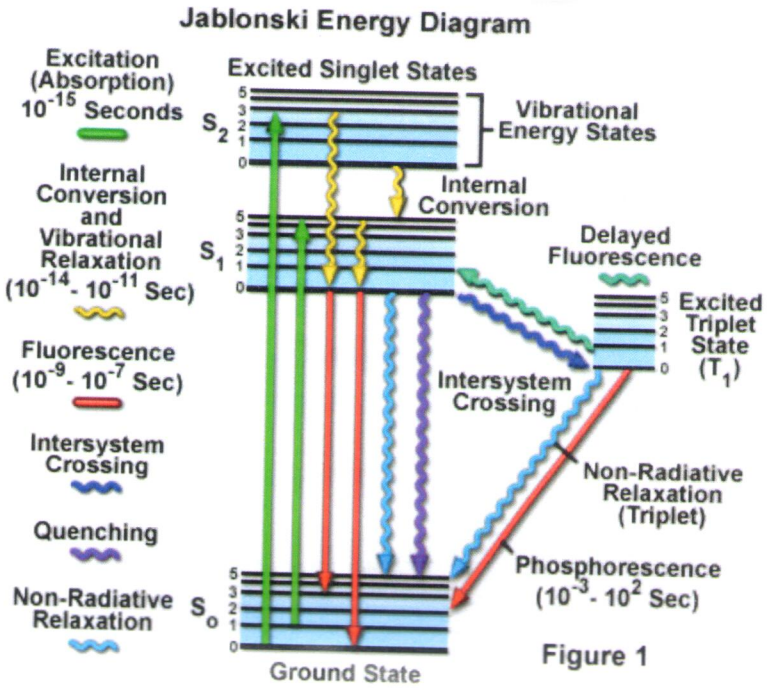
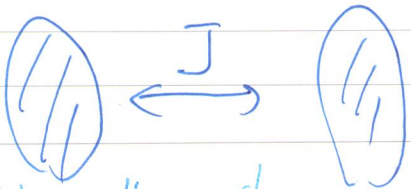


Figure 1

* multichromophoric systems : photoexcitation as

we focus on EET here but the two frameworks are similar!!

"excitons", excitation energy transfer.



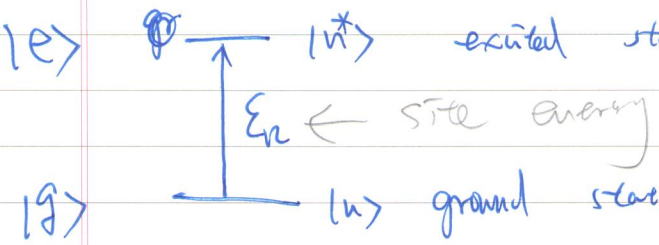
"charges", charge transfer.

$A^- + B \rightarrow A + B^-$

⇐ ~~Redfield Σ_n, p.~~ first.

* Frenkel exciton model:

⇒ We treat each chromophore as a two level system., $|n\rangle$ & $|n^*\rangle$,



In principle

We will use dimer as an example, but it can be generalized to multiple molecules.

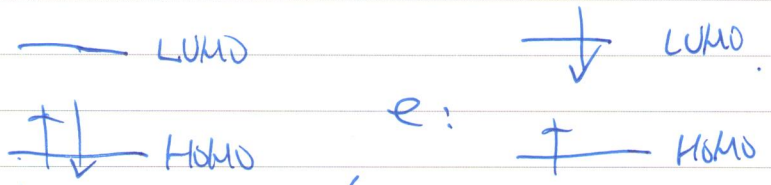
Some terms:

* exciton: electron-hole pair.

* ~~Exc~~ Frenkel exciton: bound electron-hole pair, also called tight-binding exciton.

In molecular system, separation of e^- & h^+ requires large energy (>a.e.V), so Frenkel exciton is a good representation.

This can be related to the familiar MO picture in a "frozen orbital" approx:



→ suitable when the couplings are small.

Within the Frenkel exciton model, the Hamiltonian can be written as:

often focused on one-exciton manifold

$$H = \begin{pmatrix} & |1\rangle & |1^*2\rangle & |1 2^*\rangle & |1^*2^*\rangle \\ \langle 1| & \varepsilon_g & 0 & 0 & X \\ \langle 1^*2| & 0 & \varepsilon_1 & J_{12} & X \\ \langle 1 2^*| & 0 & J_{21} & \varepsilon_2 & X \\ \langle 1^*2^*| & X & X & X & \varepsilon_1+\varepsilon_2 \end{pmatrix} \approx \begin{pmatrix} \varepsilon_1 & J_{12} \\ J_{21} & \varepsilon_2 \end{pmatrix}$$

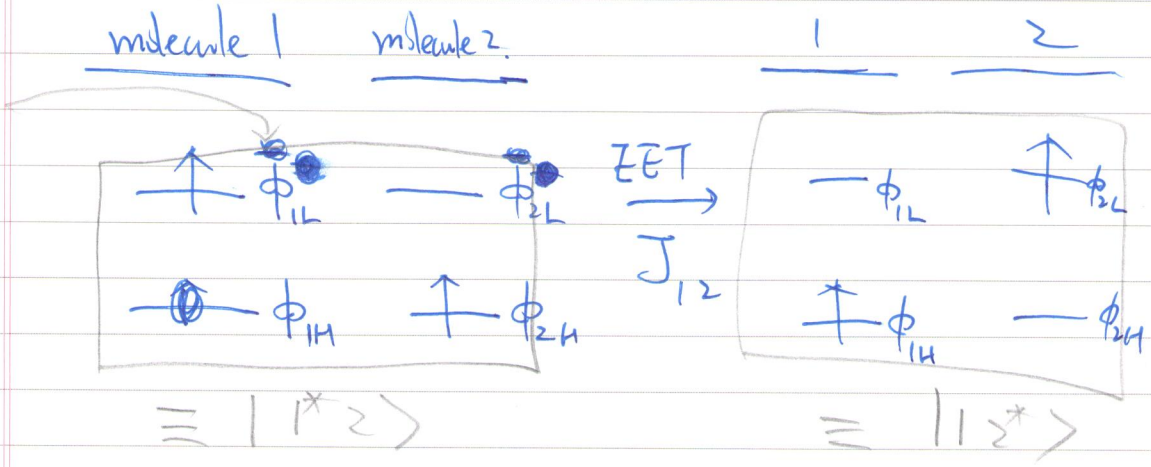
ε_n : site energies (transition energies).

J_{12} : electronic couplings.

Question now is: What is J ??

$\langle 1^* 2 | \hat{H} | 1^* 2 \rangle$

The nature of the "electronic coupling" is best understood within the two-electron, four-orbital model:

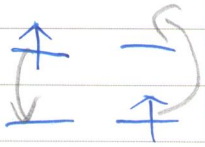


$$J_{12} = \langle 1^* 2 | \hat{H} | 1 2^* \rangle = \frac{1}{2}\{[\phi_{1L}(1)\,\phi_{2H}(2) - \phi_{1L}(1)\,\phi_{2H}(1)]\times \hat{H} \times [\phi_{1H}(1)\,\phi_{2L}(2) - \phi_{1H}(2)\,\phi_{2L}(1)]\}$$

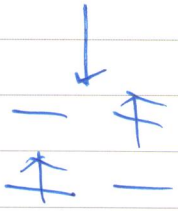
$$= \int \phi_{1L}^*(1)\,\phi_{1H}(1)\cdot\frac{1}{r_{12}}\,\phi_{2H}^*(2)\,\phi_{2L}(2)\cdot d\tau_1 d\tau_2 \quad \text{(Coulomb / (Förster))}$$

$$- \int \phi_{1L}^*(1)\,\phi_{2L}(1)\,\frac{1}{r_{12}}\,\phi_{2H}^*(2)\,\phi_{1H}(2)\cdot d\tau_1 d\tau_2 \quad \text{exchange / (Dexter)}$$

If we define transition density:

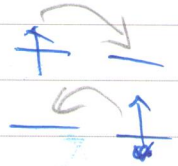


$$\rho_n(\vec{r}) = \phi_{nL}(\vec{r}) \cdot \phi_{nH}(\vec{r})$$



then the Coulomb term can be seen as Coulomb interactions between the two transition densities ⇒ can be calculated using a discrete grid method ⇒ $\int dr \to \sum_{i,j,k}$

⇒ Coulomb term often long range, can be approximated as transition-dipole–transition dipole interactions ⇒ Forster mechanism. (up to 50 Å)



⇒ The exchange term requires orbital overlap ⇒ Dexter mechanism (< 6 Å).

⇒ J_{nm} can be calculated relatively accurately using modern quantum chemistry packages (e.g. Q-Chem).

Thus, a common simple model for EET based on Frenkel excitons coupled diagonally to a harmonic bath is:

$|n\rangle$: excitation on the n-th site.

$$H_S = \sum_{n=1}^{N} \varepsilon_n |n\rangle\langle n| + \sum_{m<n} J_{nm} \cdot (|n\rangle\langle m| + |m\rangle\langle n|)$$

collective coordinate we discussed last time.

"phonon" bath.

$$H_B = \sum_\alpha \hbar\omega_\alpha \cdot b_\alpha^\dagger b_\alpha$$

dimensionless

position of phonon mode.

$$H_{SB} = \sum_{n=1,\alpha}^{N} g_{n,\alpha} \hbar\omega_\alpha \cdot |n\rangle\langle n| \cdot (b_\alpha^\dagger + b_\alpha) \equiv \sum_n |n\rangle\langle n| \hat{q}_n$$

↑ bi-linear system-bath coupling.

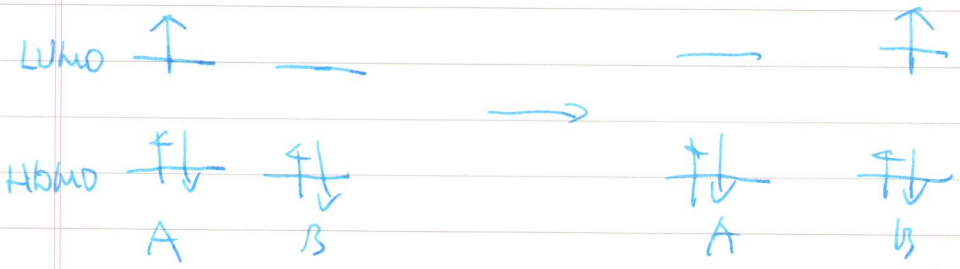
this model is successful because Gaussian fluctuations, not due to normal modes of environments.

Recall the displace oscillator or energy-gap hamiltonian that we discussed last week, this describes energy-gap of molecular excitons coupled linearly to the coordinates of a collective harmonic bath, i.e. site energies modulated by bath.

Now those are for EET, but the model for electron transfer is similar, only the "electronic coupling" term is different.

Recognize:

$$\bar{A} + B \rightarrow A + \bar{B}.$$



$$J_{12} = \int \phi_{1L}^{*}(1) \cdot \hat{H} \cdot \phi_{2L}(1)\, d\tau_1.$$

↳ single electron process!!

This is the "transfer matrix element" of the two MOs ⇒ can be calculated in a simple way, which we do not elaborate here ⇒ refer to Cherri Hsu's papers ⇒ So one model for EET & ET, with subtle differences in J & spectral density.

To describe dynamics within this model, one might based on different assumptions:

perturbative

① Weak electron–phonon coupling limit:

small H_{SB} ⇒ Redfield equation.

treat electronic part exactly, (no multi-phonon effects).

② Weak electronic coupling limit:

small J ⇒ Förster theory for EET
Marcus theory for ET.

treat system-bath part exactly.

(no coherence, electronic superposition).

This week we first consider the Redfield case, i.e. when H_{SB} is small!!

Now we recall the quantum master equation derived by using 2nd order cumulant expansion on the reduced system density matrix propagator assuming H_{SB} is "small" : $H_{SB}(t) = e^{\frac{i}{\hbar}H_0 t} \cdot H_{SB} \cdot e^{-\frac{i}{\hbar}H_0 t}$ by definition.

$H = \underbrace{H_S + H_B}_{H_0} + \underbrace{H_{SB}}_{V}$

$$\dot{\sigma}(t) = -\frac{i}{\hbar}[H_S, \sigma(t)] - \int_0^t d\tau \, \mathrm{Tr}_B \Big\{ [H_{SB}(t), [H_{SB}(t-\tau), \sigma(t) \otimes \rho_B]] \Big\}$$

$\sigma(t)$

This is a "time-local" QME, we need to plug in explicitly H_{SB} and perform the thermal average to yield the equations of motion for the reduced density matrix of the excitonic system.

Recall

$$H_{SB} = \sum_n |n\rangle\langle n| \cdot q_n .$$

The "kernel"

$$\mathrm{Tr}_B\left\{\left[H_{SB}, \left[H_{SB}(\tau-t), \sigma(t)\otimes\rho_B^{eq}\right]\right]\right\}$$

$S_m(t) = e^{\frac{i}{\hbar}H_S t}\cdot|m\rangle\langle m|\cdot e^{-\frac{i}{\hbar}H_S t}$.

$e^{\frac{i}{\hbar}H_S(\tau-t)}\cdot|m\rangle\langle m|\cdot e^{-\frac{i}{\hbar}H_S(\tau-t)} \equiv S_m(\tau-t)$.

$$= \mathrm{Tr}_B\left\{\left[\underbrace{\sum_n |n\rangle\langle n|}_{S_n} q_n, \left[\underbrace{\sum_m |m(\tau-t)\rangle\langle m(\tau-t)|}_{S_m(\tau-t)}\cdot q_m(\tau-t), \sigma(t)\otimes\rho_B^{eq}\right]\right]\right\}$$

$$= \sum_{n,m}\mathrm{Tr}_B\left\{\left[S_n q_n, \left[S_m(\tau-t) q_m(\tau-t), \sigma(t)\otimes\rho_B^{eq}\right]\right]\right\}$$

$$= \sum_{n,m}\mathrm{Tr}_B\Big\{\underbrace{S_n q_n S_m(\tau-t) q_m(\tau-t)}_{\text{system}}\cdot\underbrace{\sigma(t)\cdot\rho_B^{eq}}_{\text{bath}} - S_n q_n \sigma(t)\rho_B^{eq}\cdot S_m(\tau-t) q_m(\tau-t)$$

$$- S_m(\tau-t) q_m(\tau-t)\sigma(t)\rho_B^{eq}\cdot S_n q_n + \sigma(t)\rho_B^{eq} S_m(\tau-t) q_m(\tau-t)\cdot S_n q_n\Big\}$$

$= \langle q_n q_m(\tau-t)\rangle$ $\qquad$ $= \langle q_m(\tau-t) q_n\rangle$

Collect bath & system terms separately —

$$= \sum_{n,m}\Big\{S_n S_m(\tau-t)\sigma(t)\cdot\underbrace{\mathrm{Tr}_B\left\{q_n q_m(\tau-t)\rho_B^{eq}\right\}} - S_n\sigma(t) S_m(\tau-t)\cdot\underbrace{\mathrm{Tr}_B\left\{q_m\rho_B^{eq} q_n(\tau-t)\right\}}$$

$$- S_m(\tau-t)\sigma(t) S_n\cdot\langle q_n q_m(\tau-t)\rangle + \sigma(t) S_m(\tau-t) S_n\cdot\langle q_m(\tau-t) q_n\rangle\Big\}$$

Up to here we have seen that all the bath influence to the quantum dynamics of the

reduced-system density matrix is through

this is bath only!!

$\langle q_n q_m(\tau - t) \rangle$: time-correlation functions!!

↑ collective coordinate!!

We have studied this and showed that it can be evaluated from a spectral density function that gives the "statistics" of system-bath couplings!!

In this formalism only the time-correlations of bath fluctuations affects the system's dynamics, they play a central role in spectroscopy & statistical mechanics of non-equilibrium systems. For exciton ET problems, a "local bath" approximation is often adopted to "independent bath"

further simplify the equations:

q_n & q_m coupled to different sites, are independent:

$$\langle q_n(t) q_m(0) \rangle = \langle q_n(t) q_n \rangle \cdot \delta_{nm} \equiv C_n(t) \cdot \delta_{nm}.$$

When we learn about the Redfield theory a little bit later, i.e. we will go back to visit the QME as describe in p.14. when we discuss about Redfield theory. (Yes, that is the Redfield relaxation tensor).

~~Next wee~~

Let's summarize the main concepts introduced in this lecture:

* System-bath model & reduced-system density matrix.
* Cumulant expansion & Gaussian fluctuation model.
* quantum master equation.
* bath time-correlation ~~fu~~ functions —.

These will form the basis for all our later discussions on condensed-phase quantum dynamics & spectroscopy —.

So the kernel

$$\mathrm{Tr}_B\left\{[H_{SR}, [H_{SB}(\tau-t), \sigma(t)\otimes\rho_B^{eq}]]\right\}$$

$$= \sum_n \Big\{ C_n(t-\tau)\cdot S_n S_n(\tau-t)\sigma(t) - C_n^*(t-\tau)\cdot S_n \sigma(t) S_n(\tau-t)$$

$$- S_n(\tau-t)\sigma(t) S_n \cdot C_n(t-\tau) + C_n^*(t-\tau)\cdot \sigma(t) S_n(\tau-t)\cdot S_n \Big\}$$

(real parts)

$$= \sum_n \Big\{ C_n'(t-\tau)\cdot[S,[S(\tau-t),\sigma(t)]] + i\cdot C_n''(t-\tau)\cdot[S,[S(\tau-t),\sigma(t)]_+] \Big\}$$

(anti-commutator)

Therefore

$\tau' = t-\tau,\ d\tau' = -d\tau$

$\int_0^t d\tau = \int_t^0 -d\tau' = \int_0^t d\tau'$

$$\dot\sigma(t) = -\frac{i}{\hbar}[H_S,\sigma(t)] - \frac{1}{\hbar^2}\int_0^t d\tau \sum_n \Big\{ C_n'(t-\tau)\cdot[S_n,[S_n(\tau-t),\sigma(t)]]$$

$$+ i\, C_n''(t-\tau)\cdot[S_n,[S_n(\tau-t),\sigma(t)]_+] \Big\}$$

(dissipation)

Non-Markovian

$$= -\frac{i}{\hbar}[H_S,\sigma(t)] - \frac{1}{\hbar^2}\int_0^t d\tau \sum_n \Big\{ C_n'(\tau)\cdot[S_n,[S_n(-\tau),\sigma(t)]]$$

$$+ i C_n''(\tau)\{S_n,[S_n(-\tau),\sigma(t)]_+] \Big\}$$

Now, if $C_n'(\tau)$ decays (to zero) fast, $\tau_b \ll t$,

(energy shift)

then we can extend the integral's upper bound to ∞

In that case.

Markovian QME:

$$\dot{\sigma}(t) = \frac{-i}{\hbar}[H_S, \sigma(t)] - \frac{1}{\hbar^2}\int_0^\infty d\tau \cdot \sum_n \Big\{ C_n'(\tau)\cdot[S_n, [S_n(-\tau), \sigma(t)]] + i\, C_n''(\tau)\cdot[S_n, [S_n(-\tau), \sigma(t)]_+] \Big\}$$

memory kernel independent of t

$\Rightarrow$ Markovian QME !!

$\neq$) $-\frac{1}{\hbar^2}\int_0^\infty d\tau \cdot K(\tau)\cdot\sigma(t)$

This is a formal equation that is useful for the propagation of $\sigma(t)$ in small time steps. Most often we propagate $\sigma(t)$, i.e. integrate $\dot{\sigma}(t)$ in small time steps:

$$\sigma(t+\delta t) \approx \dot{\sigma}(t)\cdot\delta t = \frac{-i}{\hbar}[H_S, \sigma(t)]\cdot\delta t - \frac{1}{\hbar^2}\int_0^\infty d\tau \cdot K(\tau)\cdot\sigma(t)\cdot\delta t$$

Euler method →

A better way to do the propagation is to use the Crank-Nicolson method because the Liouville equation is a stiff differential system ~~~. Anyway we will not focus on this technical point.

* Redfield equation

So finally we evaluate the whole thing in the eigenbasis of H_S:

$$H_S|\alpha\rangle = \varepsilon_\alpha |\alpha\rangle$$

also define $\omega_\alpha = \frac{\varepsilon_\alpha}{\hbar}$, $\omega_{\alpha\beta} = \frac{\varepsilon_\alpha - \varepsilon_\beta}{\hbar}$

Note $|\alpha\rangle = \sum_n C_n^{(\alpha)} |n\rangle$

So $\sum_{n,\alpha\beta} = \langle\alpha|n\rangle\langle n|\beta\rangle = C_n^{\alpha *} \cdot C_n^\beta$

$$\Rightarrow \dot{\sigma}_{\alpha\beta}(t) = \langle\alpha|\dot{\sigma}(t)|\beta\rangle$$

$$= -i(\omega_\alpha - \omega_\beta)\sigma_{\alpha\beta}$$

Redfield tensor $R_{\alpha\beta;\gamma\delta}\cdot\sigma_{\gamma\delta}$

$$-\frac{1}{\hbar^2}\int_0^\infty d\tau \sum_n C_n'(\tau)\cdot\sum_{\gamma,\delta}\Big\{ e^{-i\omega_{\gamma\delta}\tau}\cdot C_n^{\alpha *} C_n^\gamma C_n^{\gamma *} C_n^\delta \cdot \sigma_{\delta\beta}(t) - e^{-i\omega_{\beta\delta}\tau}\cdot C_n^{\alpha *} C_n^{\gamma *} C_n^\delta C_n^\beta \cdot \sigma_{\gamma\delta}(t)$$

$$- e^{-i\omega_{\alpha\gamma}\tau}\cdot C_n^\alpha C_n^\gamma C_n^\delta C_n^\beta \cdot \sigma_{\gamma\delta}(t) + e^{-i\omega_{\gamma\delta}\tau}\cdot C_n^\gamma C_n^\delta C_n^\delta C_n^\beta \cdot \sigma_{\alpha\gamma}(t)\Big\}$$

$$-\frac{i}{\hbar^2}\int_0^\infty d\tau \sum_n C_n''(\tau)\cdot\sum_{\gamma,\delta}\Big\{ e^{-i\omega_{\gamma\delta}\tau}\cdot C_n^\alpha C_n^\gamma C_n^\gamma C_n^\delta \cdot \sigma_{\delta\beta}(t) + e^{-i\omega_{\beta\delta}\tau}\cdot C_n^\alpha C_n^\gamma C_n^\delta C_n^\beta \cdot \sigma_{\gamma\delta}(t)$$

$$- e^{-i\omega_{\alpha\gamma}\tau}\cdot C_n^\alpha C_n^\gamma C_n^\delta C_n^\beta \cdot \sigma_{\gamma\delta}(t) + e^{-i\omega_{\gamma\delta}\tau}\cdot C_n^\gamma C_n^\delta C_n^\delta C_n^\beta \cdot \sigma_{\alpha\gamma}(t)\Big\}$$

$$\dot{\sigma}_{\alpha\beta}(t) = -i(\omega_\alpha - \omega_\beta)\sigma_{\alpha\beta}(t) + \sum_{\gamma,\delta} R_{\alpha\beta;\gamma\delta}\cdot\sigma_{\gamma\delta}(t)$$

This equation describes various dynamics on the eigenstates of the excitonic system, including population terms & coherence terms in the reduced density matrix.

① population transfer : $R_{aa;bb}$ describes energy transfer from $|b\rangle \rightarrow |a\rangle$. $(a \neq b)$.
often negative, i.e. decrease.

② dephasing : $R_{ab;ab}$, $a \neq b$, dephasing of ρ_{ab}.

③ population to coherence transfer : $R_{ab;aa}$, $R_{ab;bb}$, $R_{ab;cc}$ ...

④ coherence transfer : $R_{ab;cd}$, $R_{ab;cb}$, $R_{ab;ac}$ ...

Note that ③ & ④ are often much smaller than ① & ② considering the stationary phase condition for the integral, so we often neglect ③ & ④ and only consider ① & ② → secular approximation.

Finally, let's focus on the population transfer term: $|b\rangle \rightarrow |a\rangle$.

$\therefore \quad \alpha = \beta = a, \quad \gamma = \delta = b$

We obtain:

$$k_{a\leftarrow b} = \frac{2}{\hbar^2}\int_0^\infty d\tau \cdot \sum_n C_n(\tau) \cdot e^{i\omega_{ba}\tau} \cdot C_n^{a*} C_n^b C_n^{b*} C_n^a$$

$$= \frac{2}{\hbar^2}\int_0^\infty d\tau \cdot \sum_n |C_n^a|^2 |C_n^b|^2 \cdot C_n(\tau) \cdot e^{i\omega_{ba}\tau}$$

assume identical bath, so $C_n(\tau)$ is independent of n, $C_n(\tau) = C(\tau)$

$$= \frac{2}{\hbar^2}\sum_n |C_n^a|^2 |C_n^b|^2 \cdot \int_0^\infty d\tau \cdot C_n(\tau) \cdot e^{i(\omega_b - \omega_a)\tau}$$

$$= \frac{2}{\hbar^2}\sum_n |C_n^a|^2 |C_n^b|^2 \cdot \int_0^\infty d\tau\, C(\tau) \cdot e^{i(\omega_b - \omega_a)\tau}$$

$$= \frac{1}{\hbar^2}|S_{ab}|^2 \cdot \mathrm{Re}\cdot\left[\int_0^\infty d\tau \cdot C(\tau) \cdot e^{i(\omega_b - \omega_a)\tau}\right]$$

$$= \frac{1}{\hbar^2}|S_{ab}|^2 \cdot \mathrm{Re}\cdot \tilde{C}(\omega_b - \omega_a).$$

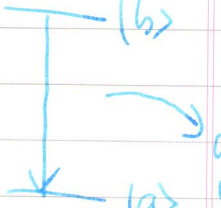
where $|S_{ab}|^2 = \sum_n |C_n^a|^2 |C_n^b|^2$ is the overlap factor between excitons $|a\rangle$ & $|b\rangle$.

$\tilde{C}(\omega)$ is the F.T. of the time correlation function: $C(t) = \langle \xi(t)\xi \rangle$.

$\tilde{C}(\omega)$ is basically the power spectrum of the bath induced site-energy fluctuations, $\tilde{C}(\omega_b - \omega_a)$ gives the "coupling strength" of the phonon modes satisfying the energy gap between the two states. So, Redfield rate is determined by

① spatial overlap of exciton wavefunctions (contributions of shared modes).
↳ must coupled to the same mode for energy dissipation.

② $\tilde{C}(\omega_b - \omega_a)$, availibility of phonon mode at the energy gap. This is a single phonon process only.



dump energy $\omega_b - \omega_a$ to a phonon mode.

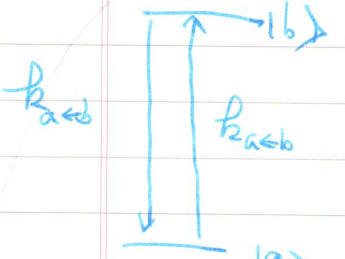
it turns out this is the biggest problem of the Redfield equation.

Similarly

$$k_{b\leftarrow a} = \frac{1}{\hbar^2}|S_{ab}|^2 \cdot \tilde{C}(\omega_a - \omega_b).$$

Therefore

$$\frac{k_{a\leftarrow b}}{k_{b\leftarrow a}} = \frac{\tilde{C}(\omega_b - \omega_a)}{\tilde{C}(\omega_a - \omega_b)} = e^{\beta\hbar(\omega_b - \omega_a)}.$$



This guarantees that in the long-time limit, the population distribution satisfies the Boltzmann distribution

$\Rightarrow$ detailed balance.

proof given in @additional material given in the last lecture (on CTIBA).

The Redfield eq. was initially introduced to treat NMR spin systems in a phenomenological way. Here we provide a microscopic derivation based on the weak system-bath interaction approximation.