

A winter short course 2014

2014/2/7.

①

Lecture 5: Excitation Energy Transfer.

* Exciton Hamiltonian.

* Driving force for energy transfer & electron transfer

* Redfield theory

* Population dynamics & detailed balance.

So, welcome back — Happy Lunar New Year!!

In the last lecture we discussed properties of

time-correlation functions. You will soon see that they

are useful. This lecture, finally, we approach

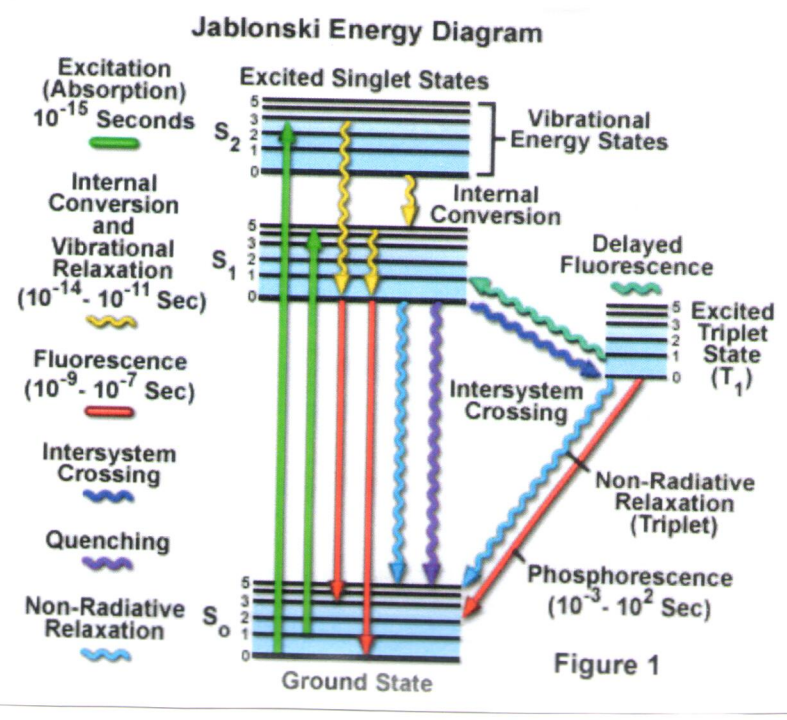
real physical problems & what we set out to

do is dissipative dynamics, with focus on ZFT & ET,

in molecular systems.

* Energy relaxation in molecular systems

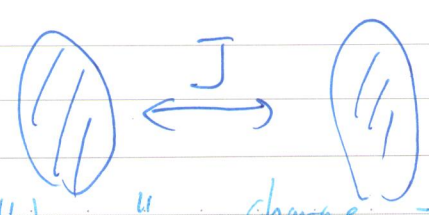
* single chromophore: vibrational relaxation / internal conversion / intersystem crossing . . .



* multichromophoric systems: photoexcitation as

We focus on EET here
the two frameworks are similar!!

"excitons", excitation energy transfer.



"charge s", charge transfer.



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← Redfield Σ_f , p. 9 ~~first~~.

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* Franck exciton model:

⇒ We treat each chromophore as

a two level system, $|n\rangle$ & $|n^*\rangle$,

$|e\rangle$  excited state ← lowest

E_n ← site energy

$|g\rangle$ $|n\rangle$ ground state of n -th molecule.

in principle

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

Some terms:

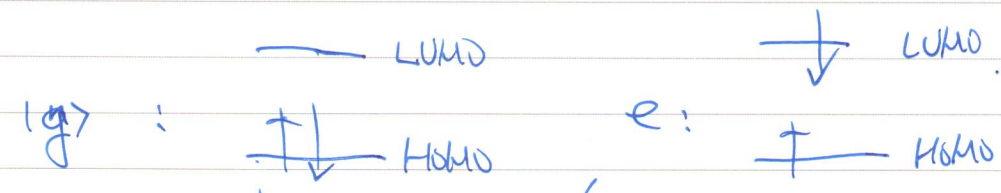
* exciton: electron-hole pair.

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

In molecular system, separation of e^- & h^+ requires
large energy ^($> 20 eV$), so Franck exciton is a good representation.

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



\Rightarrow suitable when the couplings are small.

Within the Frenkel exciton model, the

Hamiltonian can be written as:

$$H = \begin{pmatrix}
 |1\rangle & |1^*\rangle & |12\rangle & |12^*\rangle \\
 \begin{matrix} E_g \\ 0 \\ 0 \\ X \end{matrix} & \begin{matrix} 0 \\ E_1 \\ J_{12} \\ J_{21} \\ X \end{matrix} & \begin{matrix} 0 \\ J_{12} \\ E_2 \\ X \end{matrix} & \begin{matrix} X \\ X \\ X \\ E_1 + E_2 \end{matrix}
 \end{pmatrix} \approx \begin{pmatrix}
 E_1 & J_{12} \\
 J_{21} & E_2
 \end{pmatrix}$$

often focused on one-exciton manifold

E_n : site energies (transition energies).

J_{12} : electronic couplings.

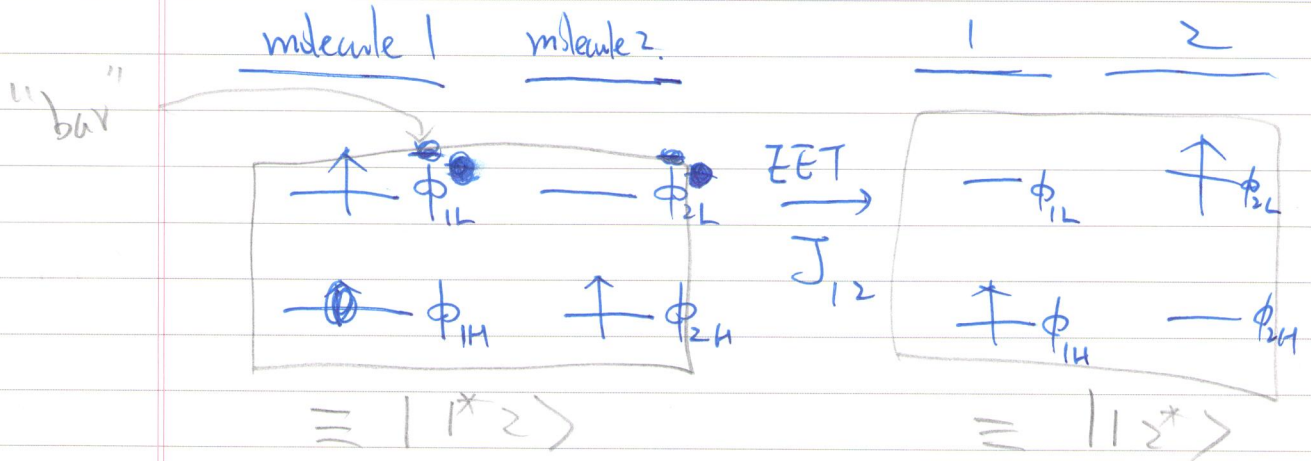
Question now is: what is J ??

$$\langle 1^*_2 | \hat{H} | 1^*_2 \rangle$$

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The nature of the "electronic coupling"

is best understood within the two-electron, four-orbital model:



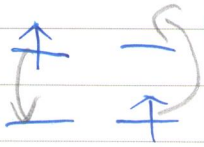
$$J_{12} = \langle 1^*_2 | \hat{H} | 1^*_1 \rangle = \frac{1}{2} \left\{ [\phi_{1L}(1) \phi_{2H}(2) - \phi_{1L}(1) \phi_{2H}(1)] \times \hat{H} \right. \\ \left. \times [\phi_{1H}(1) \phi_{2L}(2) - \phi_{1H}(2) \phi_{2L}(1)] \right\}$$

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

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If we define transition density:



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



then the Coulomb term can be seen as Coulomb interactions between the two

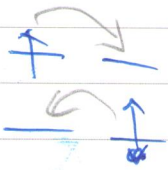
transition densities \Rightarrow can be calculated

using a discrete grid method $\Rightarrow \int dr \rightarrow \sum_{i,j,k,h}$

\Rightarrow Coulomb term often long range, can be

approximated as transition-dipole-transition dipole

interactions \Rightarrow Forster mechanism. (up to 50 Å)



\Rightarrow ~~Dexter~~ The exchange term requires

orbital overlap \Rightarrow Dexter mechanism (< 6 Å).

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

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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.

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

collective coordinate we described last time.

"phonon" bath.

$$H_B = \sum_{\alpha} \hbar \omega_{\alpha} b_{\alpha}^{\dagger} b_{\alpha}$$

dimensionless

position of phonon mode.

this model is successful

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

si-linear system-bath coupling?

because Gaussian fluctuations, not due to normal modes of environments.

Recall the displaced oscillator or energy-gap

hamiltonian that we discussed last week,

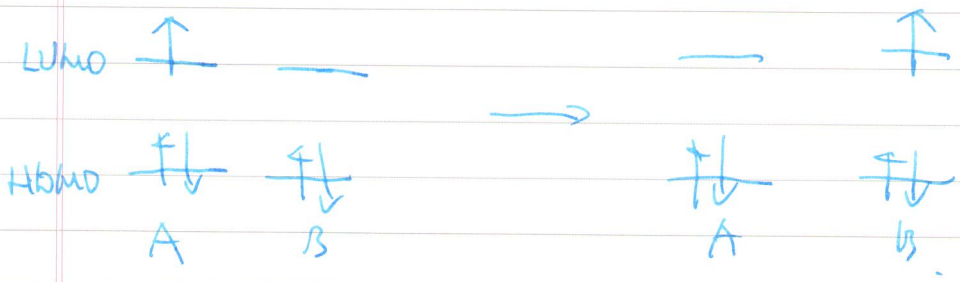
this describes energy-gap of molecular excitations

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 !



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

↑ single electron process !!

This is the "transfer matrix element" of the two MOs which can be calculated in a simple way, which we do not elaborate

So ^{one} here refer to Cheri Hsu's papers → model for EET & ET, with subtle differences in J & spectral density.

To describe dynamics within this model,
one ~~can~~ ^{might} be based on ~~a~~ different assumptions:

perturbative

① Weak electron-phonon coupling limit:

small H_{sp} \Rightarrow Redfield equation.

treat electronic part exactly,
(no multiphonon effects).

② Weak electronic coupling limit:

small J \Rightarrow 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_{sp} 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": $H_{SB} = e^{-\frac{iH_S t}{\hbar}} H_{SB} e^{\frac{iH_S t}{\hbar}}$ by definition.

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

$$\dot{\sigma}(t) = -\frac{i}{\hbar} [H_S, \sigma(t)] - \int_0^t dt' T_{\frac{H_{SB}}{\hbar}} \left\{ [H_{SB}(s), [H_{SB}(t-t'), \sigma(t)]] \right\}$$

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 exciton system.

Recall

$$H_{sb} = \sum_n |n\rangle\langle n| \cdot g_n$$

The "kernel"

$$\begin{aligned} & \text{Tr}_b \left\{ [H_{sb}, [H_{sb}(z-t), \sigma(t) \otimes \rho_b^{eq}]] \right\} \\ S_m(t) &= e^{\frac{i}{\hbar} H_{st}} \cdot |m\rangle\langle m| \cdot e^{-\frac{i}{\hbar} H_{st}} \\ &= \text{Tr}_b \left\{ \left[\sum_n |n\rangle\langle n| g_n, \left[\sum_m |m\rangle\langle m| \langle m| \otimes \langle m| \cdot g_m \cdot |m\rangle\langle m| \cdot e^{-\frac{i}{\hbar} H_s(z-t)} \cdot |m\rangle\langle m| \cdot e^{\frac{i}{\hbar} H_s(z-t)} \right], \sigma(t) \otimes \rho_b^{eq} \right] \right\} \\ &= \sum_{n,m} \text{Tr}_b \left\{ \left[S_n g_n, \left[S_m \langle m| \otimes \langle m| g_m |m\rangle\langle m| \right], \sigma(t) \otimes \rho_b^{eq} \right] \right\} \\ &= \sum_{n,m} \text{Tr}_b \left\{ \underbrace{S_n g_n}_{\text{system}} \underbrace{S_m \langle m| \otimes \langle m| g_m |m\rangle\langle m|}_{\text{bath}} \cdot \sigma(t) \cdot \rho_b^{eq} - S_n g_n \sigma(t) \rho_b^{eq} \cdot S_m \langle m| \otimes \langle m| g_m |m\rangle\langle m| \right. \\ & \quad \left. - S_m \langle m| \otimes \langle m| g_m |m\rangle\langle m| \sigma(t) \rho_b^{eq} \cdot S_n g_n + \sigma(t) \rho_b^{eq} \cdot S_m \langle m| \otimes \langle m| g_m |m\rangle\langle m| \cdot S_n g_n \right\} \\ &= \sum_{n,m} \left\{ S_n S_m \langle m| \otimes \langle m| \cdot \text{Tr}_b \left\{ \underbrace{g_n g_m}_{\text{system}} \cdot \rho_b^{eq} \right\} - S_n \sigma(t) S_m \langle m| \otimes \langle m| \cdot \text{Tr}_b \left\{ \underbrace{g_n g_m}_{\text{system}} \cdot \rho_b^{eq} \right\} \right. \right. \\ & \quad \left. \left. - S_m \langle m| \otimes \langle m| \sigma(t) S_n \cdot \langle g_n g_m \rangle + \sigma(t) S_m \langle m| \otimes \langle m| S_n \cdot \langle g_m \rangle \langle g_n \rangle \right\} \right\} \end{aligned}$$

Collect bath & system terms separately -

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

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reduced-system density matrix ρ_B through

← this ρ_B bath only!!

$\langle \hat{q}_n \hat{q}_m(t-t) \rangle$: 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 example ZET problems,

a "local bath" approximation is often adopted to

further simplify the equations:

\hat{q}_n & \hat{q}_m coupled to different sites, ~~are~~ are independent:

$$\langle \hat{q}_n(t) \hat{q}_m(t') \rangle = \langle \hat{q}_n(t) \hat{q}_n \rangle \cdot \delta_{nm} \equiv C_n(t) \cdot \delta_{nm}.$$

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When we learn about the Redfield theory

to a little bit later, i.e. we will go

back to visit the QME as describe in

P.14. ~~13~~ when we discuss about Redfield theory,

(Yes, that is the Redfield relaxation tensor).

~~Next we~~

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 functions —

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

So the kernel

$$\begin{aligned} & \text{Tr}_n \{ [H_{0n}, [H_{0n}(t-t), \sigma(t) \otimes \rho_b^{eq}]] \} \\ &= \sum_n \{ C_n(t-t) \cdot S_n S_m(t-t) \sigma(t) - C_n^*(t-t) \cdot S_n \sigma(t) S_m(t-t) \\ & \quad - S_m(t-t) \sigma(t) S_n \cdot C_n(t-t) + C_n^*(t-t) \cdot \sigma(t) S_m(t-t) \cdot S_n \} \\ &= \sum_n \{ C_n'(t-t) \cdot [S, [S(t-t), \sigma(t)]] + i \cdot C_n''(t-t) \cdot [S, [S(t-t), \sigma(t)]]_+ \} \end{aligned}$$

Therefore

$$\begin{aligned} \dot{\sigma}(t) = & -\frac{i}{\hbar} [H_s, \sigma(t)] - \frac{1}{\hbar^2} \int_0^t d\tau \sum_n \{ C_n'(t-\tau) \cdot [S_n, [S_n(\tau-t), \sigma(t)]] \\ & + i C_n''(t-\tau) \cdot [S_n, [S_n(\tau-t), \sigma(t)]]_+ \} \end{aligned}$$

Non-Markovian

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

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

Now, if $C_n(t)$ decays fast, $\tau_0 \ll t$,

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

In that case.

Markovian QMZE:

$$\dot{\sigma}(t) = \frac{1}{\hbar} [H_S, \sigma(t)] - \frac{1}{\hbar^2} \int_0^\infty dz \cdot \Sigma \left\{ C_n'(z) \cdot [S_n, [S_n(z), \sigma(t)]] \right. \\ \left. + i C_n''(z) \cdot [S_n, [S_n(z), \sigma(t)]] \right\}$$

memory kernel independent of t
 ⇒ Markovian QMZE !!
 ⇒ $-\frac{1}{\hbar^2} \int_0^\infty dz \cdot K(z) \cdot \sigma(t)$

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

Euler method →

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

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 issue.

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* Redfield equation

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

$$H_S |\alpha\rangle = E_\alpha |\alpha\rangle$$

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

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

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

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

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

Redfield tensor

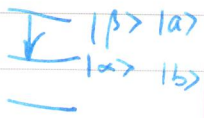
$R_{\alpha\beta;\gamma\delta} \cdot \sigma_{\gamma\delta}$

$$\left[\begin{aligned} & -\frac{1}{\hbar^2} \int_0^\infty dt \sum_n C_n(t) \cdot \sum_{\gamma\delta} \left\{ e^{-i\omega_{\alpha\beta}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) - e^{-i\omega_{\beta\alpha}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) \right. \\ & \quad \left. - e^{-i\omega_{\alpha\beta}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) + e^{-i\omega_{\beta\alpha}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) \right\} \\ & -\frac{i}{\hbar^2} \int_0^\infty dt \sum_n C_n(t) \cdot \sum_{\gamma\delta} \left\{ e^{-i\omega_{\alpha\beta}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) + e^{-i\omega_{\beta\alpha}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) \right. \\ & \quad \left. - e^{-i\omega_{\alpha\beta}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) + e^{-i\omega_{\beta\alpha}t} \cdot C_n^{\alpha*} C_n^{\beta*} C_n^\gamma C_n^\delta \cdot \sigma_{\gamma\delta}(t) \right\} \end{aligned} \right]$$

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

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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 $|b\rangle \rightarrow |a\rangle$. ($a \neq b$)

② dephasing : $R_{ab;ab}$, dephasing of ρ_{ab} .
often negative, i.e. decrease.

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

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

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 \Rightarrow secular approximation.

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

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

We obtain:

$$R_{a \leftarrow b} = \frac{2}{\hbar^2} \int_0^\infty dt \cdot \sum_n C_n(t) \cdot e^{i\omega_{ba}t} \cdot C_n^{\alpha^*} C_n^{\beta} C_n^{\gamma^*} C_n^{\delta}$$

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

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

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

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

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

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:

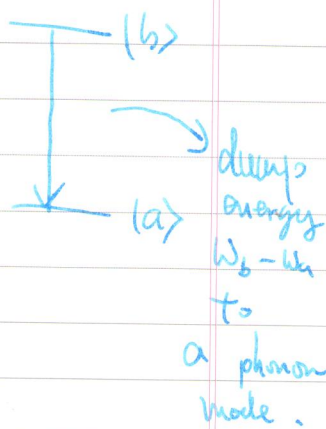
$$\tilde{C}(\omega) = \langle \hat{q}(t) \hat{q} \rangle$$

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$\tilde{C}(\omega)$ 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 satisfies the energy gap between the two states. So Redfield rate is determined by

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

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



single phonon process only.

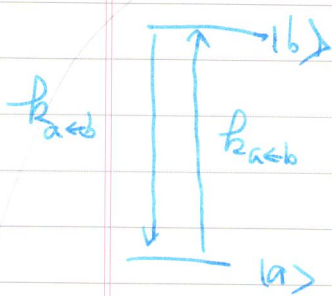
it turns out this is the biggest problem of the Redfield equation.

Similarly

$$k_{b \leftarrow a} = \frac{1}{\hbar^2} |S_{ab}|^2 \tilde{C}(W_a - W_b)$$

Therefore

$$\frac{k_{a \leftarrow b}}{k_{b \leftarrow a}} = \frac{\tilde{C}(W_b - W_a)}{\tilde{C}(W_a - W_b)} = e^{\beta \hbar (W_b - W_a)}$$



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

⇒ detailed balance.

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

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.