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Chris Engelbrecht summer school Lecture 2





 $\hat{H}_{\mathrm{mol}} = (\hat{H}_{\mathrm{el}} + \hat{H}_{\mathrm{nuc}})$





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$$\hat{H}_{\text{mol}} = \hat{H}_{\text{el}} + \hat{H}_{\text{nuc}}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1 \ m \neq n}}^{N} \sum_{\substack{m=1 \ m \neq n}}^{N} J_{mn} |m\rangle \langle n|$$

$$\int \text{change of basis}$$

$$\hat{H}_{S} = \sum_{\alpha=1}^{N} \varepsilon_{\alpha} |\alpha\rangle \langle \alpha|$$

$$\alpha\rangle = \sum_{n=1}^{N} c^{n\alpha} |n\rangle$$



 $\hat{H}_{\mathrm{mol}} = \hat{H}_{\mathrm{el}} + \hat{H}_{\mathrm{nuc}}$













 $\hat{H}_{\rm mol} = \hat{H}_{\rm el} + \hat{H}_{\rm nuc}$ ✓ ?



$$\hat{H}_{\rm mol} = \hat{H}_{\rm el} + \hat{H}_{\rm nuc}$$



$$\sum_{k=1}^{\infty} \frac{\omega_k}{2} \left[\left(\hat{p}_k^2 + \hat{q}_k^2 \right) \left| g \right\rangle \left\langle g \right| \right]$$

 $\hat{H}_{\rm mol} = \hat{H}_{\rm el} + \hat{H}_{\rm nuc}$

$$\hat{H}_{\text{nuc}} = \sum_{k=1}^{\infty} \frac{\omega_k}{2} \left[\left(\hat{p}_k^2 + \hat{q}_k^2 \right) |g\rangle \langle g| + \left(\hat{p}_k^2 + (\hat{q}_k - d_k)^2 \right) |e\rangle \langle e| \right]$$





, Open Quantum Systems $\hat{H}_{mol} = \hat{H}_{S} + \hat{H}_{B} + \hat{H}_{SB}$

we want this form

we already know:

$$\hat{H}_{\rm S} = \hat{H}_{\rm el}$$

what about

$$\hat{H}_{\rm B} + \hat{H}_{\rm SB}$$

$$\hat{H}_{mol} = \hat{H}_{el} + \hat{H}_{nuc}$$

$$\hat{H}_{\text{nuc}} = \sum_{k=1}^{\infty} \frac{\omega_k}{2} \left[\left(\hat{p}_k^2 + \hat{q}_k^2 \right) |g\rangle \langle g| + \left(\hat{p}_k^2 + (\hat{q}_k - d_k)^2 \right) |e\rangle \langle e| \right]$$
$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \hat{H}_{\text{S}} = \hat{H}_{\text{el}}$$





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$$\hat{H}_{mol} = \hat{H}_{el} + \hat{H}_{nuc}$$

$$\hat{H}_{\mathbf{S}} = \hat{H}_{\mathbf{el}}$$
$$\hat{H}_{\mathrm{nuc}} = \sum_{k=1}^{\infty} \frac{\omega_k}{2} \left[\left(\hat{p}_k^2 + \hat{q}_k^2 \right) |g\rangle \langle g| + \left(\hat{p}_k^2 + (\hat{q}_k - d_k)^2 \right) |e\rangle \langle e| \right]$$

$$\hat{H}_{\rm B} = \sum_{k=1}^{\infty} \frac{\omega_k}{2} (\hat{p}_k^2 + \hat{q}_k^2)$$

~

$$\hat{H}_{\rm SB} = -\sum_{k=1}^{\infty} \sum_{n=1}^{N} \omega_k d_{k,nn} \hat{q}_k \left| n \right\rangle \left\langle n \right|$$



$$\lambda_n = \sum_{k=1}^{\infty} \frac{\omega_k}{2} d_{k,nn}^2$$

$$\hat{H}_{mol} = \hat{H}_{el} + \hat{H}_{nuc}$$

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Statement and a second s

$$\begin{split} \hat{H}_{\mathrm{S}} &= \hat{H}_{\mathrm{el}} \\ \hat{H}_{\mathrm{nuc}} &= \sum_{k=1}^{\infty} \frac{\omega_{k}}{2} \left[\left(\hat{p}_{k}^{2} + \hat{q}_{k}^{2} \right) \left| g \right\rangle \left\langle g \right| + \left(\hat{p}_{k}^{2} + \left(\hat{q}_{k} - d_{k} \right)^{2} \right) \left| e \right\rangle \left\langle e \right| \right] \\ \hat{H}_{\mathrm{B}} &= \sum_{k=1}^{\infty} \frac{\omega_{k}}{2} \left(\hat{p}_{k}^{2} + \hat{q}_{k}^{2} \right) \\ \hat{H}_{\mathrm{SB}} &= -\sum_{k=1}^{\infty} \sum_{n=1}^{N} \omega_{k} d_{k,nn} \hat{q}_{k} \left| n \right\rangle \left\langle n \right| \\ \lambda_{n} &= \sum_{k=1}^{\infty} \frac{\omega_{k}}{2} d_{k,nn}^{2} \\ \end{split}$$
Nuclear motion

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} |m\rangle \langle n|$$

$$\hat{H}_{\rm B} = \sum_{k=1}^{\infty} \frac{\omega_k}{2} (\hat{p}_k^2 + \hat{q}_k^2).$$

$$\hat{H}_{\rm SB} = -\sum_{k=1}^{\infty} \sum_{n=1}^{N} \omega_k d_{k,nn} \hat{q}_k |n\rangle \langle n| \qquad |e\rangle \stackrel{\uparrow}{\downarrow} \stackrel{\downarrow}{\downarrow} \stackrel{$$



 $\lambda_n = \sum_{k=1}^{\infty} \frac{\omega_k}{2} d_{k,nn}^2.$

Nuclear motion



Open Quantum Systems

$$\hat{H}_{\rm mol} = \hat{H}_{\rm S} + \hat{H}_{\rm B} + \hat{H}_{\rm SB}$$

What can we do with this description?



Open Quantum Systems

$$\hat{H}_{\rm mol} = \hat{H}_{\rm S} + \hat{H}_{\rm B} + \hat{H}_{\rm SB}$$

What can we do with this description?

1. How excitation energy is transferred

Open Quantum Systems

$$\hat{H}_{\rm mol} = \hat{H}_{\rm S} + \hat{H}_{\rm B} + \hat{H}_{\rm SB}$$

What can we do with this description?



How excitation energy is transferred
 Spectroscopy

 $\hat{H}_{\rm mol} = \hat{H}_{\rm S} + \hat{H}_{\rm B} + \hat{H}_{\rm SB}$

What can we do with this description?

How excitation energy is transferred
 Spectroscopy





$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}}$$

$$\hat{H}_{\text{S}} = \sum_{n=1}^{N} \varepsilon_n |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \quad \text{(perturbation)}$$

First order perturbation theory: $k_{m \to n} = \frac{\pi}{2\hbar} |J_{mn}|^2 \rho(E)$ Fermi's golden rule



$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}}$$

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Förster theory



Förster theory









Förster theory







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First order perturbation theory:

$$k_{m \to n} = \frac{\pi}{2\hbar} |J_{mn}|^2 \rho(E)$$
 Fermi's golden rule
We arrive at the **Förster** equation:
$$k_{DA} \propto \left(\frac{R_0}{R}\right)^6$$
$$R_0^6 = \frac{\kappa^2}{n^4} \cdot \int \frac{\varepsilon_A(\tilde{v}) \cdot F_D(\tilde{v})}{\tilde{v}^4} d\tilde{v}$$
distance between pigments m and n

relative orientation of dipoles m and n



$$\hat{H}_{mol} = \hat{H}_{S} + \hat{H}_{B} + \hat{H}_{SB}$$
 (perturbation)
$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1 \ m \neq n}}^{N} \sum_{\substack{m=1 \ m \neq n}}^{N} J_{mn} m\rangle \langle n|$$
 strong

$$\hat{H}_{SB} = -\sum_{k=1}^{\infty} \sum_{n=1}^{N} \omega_k d_{k,nn} \hat{q}_k |n\rangle \langle n|$$

Derivation of Redfield Relaxation operator

$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

1. start with Liouville-von Neumann equation in the interaction picture

$$\frac{\partial}{\partial t} \rho'(t) = -\frac{i}{\hbar} [H_I(t), \rho'(t)].$$

$$\rho'(t) = e^{iH_0 t} \rho(t) e^{iH_0 t}$$

$$H_0 = H_S + H_B$$


start with

$$\frac{\partial \hat{\rho}^S}{\partial t} = \frac{-i}{\hbar} [\hat{H}, \hat{\rho}^S]$$

For any operator, we can go from the Schrödinger to interaction picture using

$$\hat{A}'(t) = e^{i\hat{H}_0 t/\hbar} \hat{A}^S e^{-i\hat{H}_0 t/\hbar}$$

Doing this for $\hat{\rho}^{I}(t)$ and taking the time derivative:

$$\frac{\partial}{\partial t}\rho^{I}(t) = \frac{i}{\hbar}[H_{0},\rho^{I}] + e^{iH_{0}t/\hbar} \left(\frac{\partial}{\partial t}\rho^{S}(t)\right) e^{-iH_{0}t/\hbar}$$

substituting in the Schrödinger-picture Liouville equation:

$$rac{\partial}{\partial t}
ho'(t)=rac{i}{\hbar}[H_0,
ho']+e^{iH_0t/\hbar}\Big(-rac{i}{\hbar}[H_0+H_I,
ho]\Big)e^{-iH_0t/\hbar}.$$

which gives

$$\frac{\partial}{\partial t}\rho'(t) = \frac{i}{\hbar}[H_0,\rho'] - \frac{i}{\hbar}[H_0,\rho'] + e^{iH_0t/\hbar} \left(-\frac{i}{\hbar}[H_I,\rho]\right) e^{-iH_0t/\hbar},$$

$$\frac{\partial}{\partial t} \rho'(t) = e^{iH_0t/\hbar} \left(-\frac{i}{\hbar}[H_I,\rho]\right) e^{-iH_0t/\hbar},$$

after calculating the commutator, we obtain

$$\frac{\partial}{\partial t}\rho'(t) = -\frac{i}{\hbar}[H_I(t),\rho'(t)].$$



time-dependence mean interaction picture



$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

1. start with Liouville-von Neumann equation in the interaction picture

$$\frac{\partial}{\partial t}\rho'(t) = -\frac{i}{\hbar}[H_I'(t),\rho'(t)].$$

$$\rho'(t) = e^{iH_0 t} \rho(t) e^{iH_0 t}$$

$$\dot{H_0} = H_S + H_B$$



$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$

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1. start with Liouville-von Neumann equation in the interaction picture

$$\frac{\partial}{\partial t}\rho'(t) = -\frac{i}{\hbar}[H_I(t),\rho'(t)]$$

$$e^{iH_0t}H_{SB}e^{-iH_0t}$$

$$\rho'(t) = e^{iH_0 t} \rho(t) e^{-iH_0 t}$$
$$H_0 = H_S + H_B$$



$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

1. start with Liouville-von Neumann equation in the interaction picture of

$$\frac{\partial}{\partial t}\rho'(t) = -\frac{i}{\hbar}[H_I(t),\rho'(t)]$$

2. integrate and substitute back

$$\rho'(t) = \rho'(0) - \frac{i}{\hbar} \int_{0}^{t} d\tau [H_I(\tau), \rho'(\tau)]$$

$$\frac{\partial}{\partial t} \rho'(t) = -\frac{i}{\hbar} [H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_{0}^{t} d\tau [H_I(t), [H_I(\tau), \rho'(\tau)]]$$

$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

- 1. start with Liouville-von Neumann equation in the interaction picture of
 - $\frac{\partial}{\partial t}\rho'(t) = -\frac{i}{\hbar}[H_I(t),\rho'(t)]$
- 2. integrate and substitute back

$$\rho'(t) = \rho'(0) - \frac{i}{\hbar} \int_{0}^{t} d\tau [H_I(\tau), \rho'(\tau)]$$

$$\frac{\partial}{\partial t} \rho'(t) = -\frac{i}{\hbar} [H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_{0}^{t} d\tau [H_I(t), [H_I(\tau), \rho'(\tau)]]$$

3. We take the trace over the bath (we average over all bath degrees of freedom).

$$\frac{\partial}{\partial t} \rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho'(\tau)]]$$

$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \xrightarrow{\text{(perturbation)}} \hat{H}_{\text{S}} = \sum_{n=1}^{N} \varepsilon_n |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \xrightarrow{\text{strong}} \text{strong}$$

$$\frac{\partial}{\partial t}\rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho'(\tau)]]$$

- 4. make the Born approximation
 - $\rho'(\tau) = \rho'_S(\tau)\rho'_B(0)$



$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1\\m \neq n}}^{N} \sum_{\substack{m=1\\m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

$$\frac{\partial}{\partial t}\rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho'(\tau)]]$$

4. make the Born approximation

$$\frac{\partial}{\partial t}\rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho_S'(0)\rho_B'(0)] - \frac{1}{\hbar^2} \int_0^t d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho_S'(\tau)\rho_B'(0)]]$$

$$\rho'(\tau) = \rho'_S(\tau)\rho'_B(0)$$

$$\hat{H}_{mol} = \hat{H}_{S} + \hat{H}_{B} + \hat{H}_{SB} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1 \ m \neq n}}^{N} \sum_{\substack{m=1 \ m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

$$\frac{\partial}{\partial t}\rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho'(\tau)]]$$

4. make the Born approximation

5.

$$\frac{\partial}{\partial t}\rho_{S}'(t) = -\frac{i}{\hbar} \operatorname{tr}_{B}[H_{I}(t), \rho_{S}'(0)\rho_{B}'(0)] - \frac{1}{\hbar^{2}} \int_{0}^{t} d\tau \operatorname{tr}_{B}[H_{I}(t), [H_{I}(\tau), \rho_{S}'(\tau)\rho_{B}'(0)]$$
make the Markov approximation
$$\frac{\partial}{\partial t}\rho_{S}'(t) = -\frac{i}{\hbar} \operatorname{tr}_{B}[H_{I}(t), \rho_{S}'(0)\rho_{B}'(0)] - \frac{1}{\hbar^{2}} \int_{0}^{t} d\tau \operatorname{tr}_{B}[H_{I}(t), [H_{I}(\tau), \rho_{S}'(t)\rho_{B}'(0)]]$$

$$\xrightarrow{t=0}{t=1/2} t=1$$

$$\hat{H}_{mol} = \hat{H}_{S} + \hat{H}_{B} + \hat{H}_{SB} \qquad \text{(perturbation)}$$

$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1 \ m \neq n}}^{N} \sum_{\substack{m=1 \ m \neq n}}^{N} J_{mn} m\rangle \langle n| \qquad \text{strong}$$

$$\frac{\partial}{\partial t}\rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho'(\tau)]]$$

4. make the Born approximation

5.

$$\frac{\partial}{\partial t}\rho_{S}'(t) = -\frac{i}{\hbar} \text{tr}_{B}[H_{I}(t), \rho_{S}'(0)\rho_{B}'(0)] - \frac{1}{\hbar^{2}} \int_{0}^{t} d\tau \text{tr}_{B}[H_{I}(t), [H_{I}(\tau), \rho_{S}'(\tau)\rho_{B}'(0)]]$$

make the Markov approximation

$$\frac{\partial}{\partial t}\rho_S'(t) = -\frac{i}{\hbar} \operatorname{tr}_B[H_I(t), \rho_S'(0)\rho_B'(0)] - \frac{1}{\hbar^2} \int_0^{t} d\tau \operatorname{tr}_B[H_I(t), [H_I(\tau), \rho_S'(t)\rho_B'(0)]]$$

$$\frac{\partial}{\partial t}\rho_{\alpha\beta}(t) = -\frac{i}{\hbar}\omega_{\alpha\beta}\rho_{\alpha\beta}(t) - \sum_{\delta,\gamma}R_{\alpha\beta\gamma\delta}\rho_{\gamma\delta}(t), \qquad \omega_{\alpha\beta} = \varepsilon_{\alpha} - \varepsilon_{\beta}$$

$$\hat{H}_{\text{mol}} = \hat{H}_{\text{S}} + \hat{H}_{\text{B}} + \hat{H}_{\text{SB}} \qquad \text{(perturbation)}$$
$$\hat{H}_{S} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{\substack{n=1 \ m \neq n}}^{N} \sum_{\substack{m=1 \ m \neq n}}^{N} J_{mn} |m\rangle \langle n| \qquad \text{strong}$$

$$R_{\alpha\beta\gamma\delta} = -\frac{1}{\hbar^2} \int_{0}^{\infty} dt' \{\Lambda_{\delta\beta\alpha\gamma} e^{-i\omega_{\delta\beta}t'} + \Lambda_{\delta\beta\alpha\gamma} e^{-i\omega_{\alpha\gamma}t'} \}$$

$$-\delta_{\delta\beta}\sum_{s}\Lambda_{\alpha ss\gamma}e^{-i\omega_{s\gamma}t'}-\delta_{\gamma\alpha}\sum_{s}\Lambda_{\delta ss\beta}e^{-i\omega_{\delta s}t'}\Big\},$$





Based on our conceptual model of the first lecture:

- light causes oscillations in the charges of the pigment molecules
- pigment molecules interact such that excitation (by light) of one causes excitation in some others (delocalization)
- the orientation of pigment molecules determine the extent of delocalization
- nuclear motion can cause energy transfer between eigenstates (the energy is transferred to nuclear vibrations)
- nuclear motions has the form of correlated random noise; the correlation function of the charge fluctuation gives information about the frequency of the charge fluctuation as well as the nuclear vibrations.















Summary









Redfield theory





$$\frac{\partial}{\partial t} \rho_S(t)$$
$$\frac{d}{dt} P_\beta = \sum_{\alpha} k_{\beta \leftarrow \alpha} P_\alpha$$
$$k_{\beta \leftarrow \alpha} = \sum_n |c_\alpha^n|^2 |c_\beta^n|^2 C_n (\omega_\beta - \omega_\alpha)$$

other methods:

modified Redfield method: includes off-diagonal (in the exciton basis) system-bath couplings non-perturbatively. Hierarchical equations of motion: exact, in the sense that they do not require additional assumptions.



Spectroscopy



FMO



Electric field and polarization





Tomáš Mančal, Charles University, Prague

Electric field and polarization

 $\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$ $\nabla \cdot \mathbf{B} = 0$ $\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$ $\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}$

- Derivation i.t.o. potentials $B = \nabla \times A$ $E = -(\frac{\partial}{\partial t}A + \nabla \phi)$
- in the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$
- Helmholtz theorem $E = E^{\perp} + E^{\parallel}$
- Relate current density to polarization density $j^{\perp} = \frac{\partial}{\partial t} P$

$$-\nabla^2 \boldsymbol{E}^{\perp}(t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{E}^{\perp}(t) = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{P}(t)$$

Electric field and polarization

$$-\nabla^2 \boldsymbol{E}^{\perp}(t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{E}^{\perp}(t) = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{P}(t)$$

Fourier transform

$$k^2 E^{\perp}(\omega) - rac{\omega}{c^2} E^{\perp}(\omega) = -rac{\omega}{\epsilon_0 c^2} P(\omega)$$

 $P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$

Linear polarization

$$-\nabla^2 \boldsymbol{E}^{\perp}(t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{E}^{\perp}(t) = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \boldsymbol{P}(t)$$

Fourier transform

$$k^{2}E^{\perp}(\omega) - \frac{\omega}{c^{2}}E^{\perp}(\omega) = -\frac{\omega}{\epsilon_{0}c^{2}}P(\omega)$$

$$P = P_{0} + \epsilon_{0}\chi^{(1)}E + \epsilon_{0}\chi^{(2)}E^{2} + \epsilon_{0}\chi^{(3)}E^{3} + \cdots$$

Linear polarization

$$-\nabla^{2} \boldsymbol{E}^{\perp}(t) + \frac{1}{c^{2}} \frac{\partial^{2}}{\partial t^{2}} \boldsymbol{E}^{\perp}(t) = -\frac{1}{\epsilon_{0}c^{2}} \frac{\partial^{2}}{\partial t^{2}} \boldsymbol{P}(t) \qquad \left[-k^{2} + \frac{\omega^{2}}{c^{2}} (1 + \chi(\omega))\right] \boldsymbol{E}^{\perp}(\omega) = 0$$
Fourier transform
$$k^{2} \boldsymbol{E}^{\perp}(\omega) - \frac{\omega}{c^{2}} \boldsymbol{E}^{\perp}(\omega) = -\frac{\omega}{\epsilon_{0}c^{2}} \boldsymbol{P}(\omega)$$

$$P = P_{0} + \frac{\omega}{\epsilon_{0}\chi^{(1)}E} + \frac{\omega}{\epsilon_{0}\chi^{(2)}E^{2}} + \frac{\omega}{\epsilon_{0}\chi^{(3)}E^{3}} + \frac{\omega}{\epsilon_{0}\epsilon_{0}\epsilon_{0}} + \frac{\omega}{\epsilon_{0}\epsilon_{0}} + \frac{\omega}{\epsilon_{$$

Linear polarization and absorption

$$-\nabla^{2} \mathbf{E}^{\perp}(t) + \frac{1}{c^{2}} \frac{\partial^{2}}{\partial t^{2}} \mathbf{E}^{\perp}(t) = -\frac{1}{\epsilon_{0}c^{2}} \frac{\partial^{2}}{\partial t^{2}} \mathbf{P}(t)$$

$$= 0$$

$$= 0$$

$$= 0$$

$$k^{2} \mathbf{E}^{\perp}(\omega) - \frac{\omega}{c^{2}} \mathbf{E}^{\perp}(\omega) = -\frac{\omega}{\epsilon_{0}c^{2}} \mathbf{P}(\omega)$$

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$$k = \frac{\omega}{c} \sqrt{1 + \chi(\omega)} \quad \chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$

$$\mathbf{P} = \mathbf{P}_{0} + \frac{\omega}{\epsilon_{0}} \chi^{(1)} \mathbf{E} + \frac{\omega}{\epsilon_{0}} \chi^{(2)} \mathbf{E}^{2} + \frac{\omega}{\epsilon_{0}} \chi^{(3)} \mathbf{E}^{3} + \dots$$

Linear polarization and absorption

$$\nabla^{2} E^{\perp}(t) + \frac{1}{c^{2}} \frac{\partial^{2}}{\partial t^{2}} E^{\perp}(t) = -\frac{1}{\epsilon_{0}c^{2}} \frac{\partial^{2}}{\partial t^{2}} P(t)$$
Fourier transform
$$k^{2} E^{\perp}(\omega) - \frac{\omega}{c^{2}} E^{\perp}(\omega) = -\frac{\omega}{\epsilon_{0}c^{2}} P(\omega)$$

$$= 0$$

$$k = \frac{\omega}{c} \sqrt{1 + \chi(\omega)} \qquad \chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$

$$k = \frac{\omega}{c} (n + i\frac{\chi''(\omega)}{2n}) \qquad \text{with} \qquad n = \sqrt{1 + \chi'(\omega)}$$

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$$I = I_{0}e^{-\alpha(\omega)z}$$

$$I = I_{0}e^{-\alpha(\omega)z}$$

$$\alpha(\omega) = \frac{\omega}{nc}\chi''(\omega)$$

Construction of the second second

Orders of polarization

 $P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$ susceptibilities

Orders of polarization

$$P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$$

linear spectroscopy

Orders of polarization

$$P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$$
nonlinear spectroscopy

Susceptibility



P In the time domain



$$P(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + \dots$$

Response functions

$$P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$$
$$P^{(n)} = P^{(n)}(\omega)$$
$$E = E(\omega)$$
$$\chi^{(n)} = \chi^{(n)}(\omega)$$

susceptibilities

$$P(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + \dots$$

$${}^{n)}(t) = \int_{0}^{\infty} d\tau_n \int_{0}^{\infty} d\tau_{n-1} \dots \int_{0}^{\infty} d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \dots, \tau_1) E(t-\tau_n) E(t-\tau_n - \tau_{n-1}) \dots E(t-\tau_n - \tau_{n-1} - \dots - \tau_1)$$

Response functions

$$P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$$
$$P^{(n)} = P^{(n)}(\omega)$$
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susceptibilities

$$P(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + \dots$$

F

$${}^{(n)}(t) = \int_{0}^{\infty} d\tau_{n} \int_{0}^{\infty} d\tau_{n-1} \dots \int_{0}^{\infty} d\tau_{1} \mathcal{R}^{(n)}(\tau_{n}, \tau_{n-1}, \dots, \tau_{1}) E(t-\tau_{n}) E(t-\tau_{n}-\tau_{n-1}) \dots E(t-\tau_{n}-\tau_{n-1}-\dots-\tau_{1})$$

time

Response functions

$$P = P_0 + \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots$$
$$P^{(n)} = P^{(n)}(\omega)$$
$$E = E(\omega)$$
$$\chi^{(n)} = \chi^{(n)}(\omega)$$

susceptibilities

$$P(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + \dots$$

$${}^{n)}(t) = \int_{0}^{\infty} d\tau_n \int_{0}^{\infty} d\tau_{n-1} \dots \int_{0}^{\infty} d\tau_1 \underbrace{\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \dots, \tau_1)}_{\text{response function}} E(t-\tau_n) E(t-\tau_n-\tau_{n-1}) \dots E(t-\tau_n-\tau_{n-1}-\dots-\tau_1)$$

$$\chi^{(1)}(\omega) = \frac{1}{\omega} \int_{-\infty}^{\infty} \mathcal{R}^{(1)}(t) e^{i\omega t} dt$$

$$\begin{aligned}
\mathbf{Summary} \\
-\nabla^2 E^{\perp}(t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} E^{\perp}(t) = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} P(t) \\
P = P_0^{\prime} + \underbrace{\epsilon_0 \chi^{(1)} E}_{\tau^{-1} + \epsilon_0 \chi^{(2)} E^{2} + \epsilon_0 \chi^{(3)} E^3_{-} \pm \ldots}_{\pi^{-1} + \ldots} \begin{bmatrix} P^{(n)} = P^{(n)}(\omega) \\ E = E(\omega) \\ \chi^{(n)} = \chi^{(n)}(\omega) \end{bmatrix} \\
\overline{\alpha(\omega) = \frac{\omega}{nc} \chi''(\omega)} \underbrace{\chi(\omega) = \chi'(\omega) + i \chi''(\omega)}_{\chi(\omega) = \chi'(\omega) + i \chi''(\omega)} \\
P^{(n)}(t) = \int_0^{\infty} d\tau_n \int_0^{\infty} d\tau_n \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) E(t - \tau_n) E(t - \tau_n - \tau_{n-1}) \ldots E(t - \tau_n - \tau_{n-1} - \ldots - \tau_1)} \\
\overline{\chi^{(1)}(\omega) = \frac{1}{\omega} \int_{-\infty}^{\infty} \mathcal{R}^{(1)}(t) e^{i\omega t} dt}
\end{aligned}$$
Quantum Mechanics: superoperators



$$\hat{\rho} = |\Psi\rangle \langle \Psi|$$
$$\hat{\rho}(t) = \hat{U}(t) |\Psi\rangle \langle \Psi| \hat{U}^{\dagger}(t)$$
$$= \mathcal{U}(t)\hat{\rho}(0)$$

Quantum Mechanics: superoperators



 $\hat{\rho} = |\Psi\rangle \langle \Psi|$ $\hat{\rho}(t) = \hat{U}(t) |\Psi\rangle \langle \Psi| \hat{U}^{\dagger}(t)$ $= \mathcal{U}(t) \hat{\rho}(0)$ Superoperators $\mathcal{V}\hat{A} = [\hat{\mu}, \hat{A}]$

QM of response



QM of response



QM of linear response



 $\mathcal{R}^{(1)}(t) = i \mathrm{Tr}[\hat{\mu} \mathcal{U}_{\mathrm{mol}}(t) \mathcal{V} \rho^{\mathrm{eq}}]$













Absorption spectrum

$$\mathrm{S}^{\mathrm{A}}(\omega) \propto 2\mathrm{Re}\int_{0}^{\infty} dt \, e^{i\omega t} R^{(1)}(t)$$

Absorption spectrum







$$\mathbf{S}^{\mathbf{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathbf{A}} \left[2 \mathrm{Re} \int_{0}^{\infty} dt \, e^{i\omega t} \mathbf{I}_{mn}^{\mathbf{A}}(t) \right]$$

$$\mathbf{S}^{\mathbf{E}}(\omega) \propto \omega^{3} \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathbf{E}} \left[2 \operatorname{Re} \int_{0}^{\infty} dt \, e^{-i\omega t} \mathbf{I}_{mn}^{\mathbf{E}}(t) \right]$$

Summary



Summary





Absorption spectroscopy

$$\mathbf{S}^{\mathbf{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathbf{A}} \left[2 \operatorname{Re} \int_{0}^{\infty} dt \, e^{i\omega t} \mathbf{I}_{mn}^{\mathbf{A}}(t) \right]$$





Circular dichroism spectroscopy

$$\mathbf{S}^{\mathrm{CD}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} \underbrace{f_{mn}^{\mu,\mathrm{CD}}}_{0} \left[2\mathrm{Re} \int_{0}^{\infty} dt \, e^{i\omega t} \mathbf{I}_{mn}^{\mathrm{A}}(t) \right]$$



Linear dichroism spectroscopy

$$\mathbf{S}^{\mathrm{LD}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} \underbrace{f_{mn}^{\mu,\mathrm{LD}}}_{0} \left[2\mathrm{Re} \int_{0}^{\infty} dt \, e^{i\omega t} \mathbf{I}_{mn}^{\mathrm{A}}(t) \right]$$



$$f_{mn}^{\mu,\text{LD}} = \boldsymbol{\mu}_m \cdot \boldsymbol{\mu}_n - 3|\boldsymbol{\mu}_m||\boldsymbol{\mu}_n|\cos\alpha_m\cos\alpha_n$$



$$S^{A}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,A} \left[2 \operatorname{Re} \int_{0}^{\infty} dt \, e^{i\omega t} \prod_{mn}^{A}(t) \right]$$

$$\mathbf{I}_{mn}^{\mathbf{A}}(t) = \langle n | \operatorname{Tr}_{B}[e^{-i\hat{H}_{g}t}e^{i\hat{H}_{e}t}\hat{\rho}^{\mathrm{eq}}] | m \rangle$$
??

reminder

$$R^{(1)}(t) = \text{Tr}[e^{i\hat{H}_{\text{mol}}t}\hat{\boldsymbol{\mu}}e^{-i\hat{H}_{\text{mol}}t}\hat{\boldsymbol{\mu}}\hat{\rho}^{\text{eq}}] = \langle \hat{\mu}(t)\hat{\mu}(0)\rangle$$





 $|g\rangle$ ______site n





time

$$\langle \xi_n(t) \rangle = 0 \langle \xi_n(t)\xi_n(t') \rangle = C_n(t-t') \langle \xi_n(t)\xi_m(t') \rangle = 0$$

$$\mathbf{I}^{\mathbf{A}}(t) = \mathrm{Tr}_{B} \Big[\exp_{+} \big[-i \big(\hat{H}_{S} t + \int_{0}^{t} d\tau \, \hat{H}_{SB}(\tau) \big) \big] \hat{\rho}_{B}^{\mathrm{eq}} \Big],$$



Förster resonance energy transfer, absorption and emission spectra in multichromophoric systems. III. Exact stochastic path integral evaluation Jeremy M. Moix, Jian Ma, and Jianshu Cao

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$$I^{A}(t) = \operatorname{Tr}_{B}\left[\exp_{+}\left[-i\left(\hat{H}_{S}t + \int_{0}^{t} d\tau \,\hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_{B}^{\mathrm{eq}}\right],$$
$$I^{A}(t) = \operatorname{Tr}_{B}\left(e^{kt}\hat{\rho}_{B}^{\mathrm{eq}}\right)$$
$$= \langle e^{kt} \rangle_{B}$$

$$I^{A}(t) = \operatorname{Tr}_{B} \left[\exp_{+} \left[-i \left(\hat{H}_{S}t + \int_{0}^{t} d\tau \, \hat{H}_{SB}(\tau) \right) \right] \hat{\rho}_{B}^{eq} \right],$$

$$I^{A}(t) = \operatorname{Tr}_{B} \left(e^{kt} \hat{\rho}_{B}^{eq} \right)$$

$$= \langle e^{kt} \rangle_{B}$$

$$\swarrow$$

$$\left\langle \frac{d\mathcal{I}}{dt} = k\mathcal{I} \right\rangle$$

$$\begin{split} \mathbf{I}^{\mathbf{A}}(t) &= \mathrm{Tr}_{B} \Big[\exp_{+} \big[-i \big(\hat{H}_{S}t + \int_{0}^{t} d\tau \, \hat{H}_{SB}(\tau) \big) \big] \hat{\rho}_{B}^{\mathrm{eq}} \Big], \\ \mathbf{I}^{\mathbf{A}}(t) &= \mathrm{Tr}_{B} \big(e^{kt} \hat{\rho}_{B}^{\mathrm{eq}} \big) \\ &= \langle e^{kt} \rangle_{B} \\ &\swarrow \\ \begin{pmatrix} \frac{d\mathcal{I}}{dt} = k\mathcal{I} \rangle \\ &\swarrow \\ \mathbf{I}^{\mathbf{A}}(t) = -i \big(\hat{H}_{S} + \sum_{n=1}^{\infty} \xi_{n}(t) \, |n\rangle \, \langle n| \big) \mathcal{I}^{\mathbf{A}}(t) \\ &\mathbf{I}^{\mathbf{A}}(t) = \langle \mathcal{I}^{\mathbf{A}}(t) \rangle_{\xi} \end{split}$$

time

Exact method $\mathbf{I}^{\mathbf{A}}(t) = \mathrm{Tr}_{B} \Big[\exp_{+} \Big[-i \big(\hat{H}_{S} t + \int_{0}^{t} d\tau \, \hat{H}_{SB}(\tau) \big) \Big] \hat{\rho}_{B}^{\mathrm{eq}} \Big],$ $I^{A}(t) = Tr_{B}(e^{kt}\hat{\rho}_{B}^{eq})$ $= \langle e^{kt} \rangle_B$ $\left\langle \frac{d\mathcal{I}}{dt} = \mathbf{k}\mathcal{I} \right\rangle$ $\frac{d}{dt}\mathcal{I}^{\mathbf{A}}(t) = -i\left(\hat{H}_{S} + \sum_{n=1}^{\infty} \xi_{n}(t) \left|n\right\rangle \left\langle n\right|\right) \mathcal{I}^{\mathbf{A}}(t)$ $\mathbf{I}^{\mathbf{A}}(t) = \langle \mathcal{I}^{\mathbf{A}}(t) \rangle_{\mathcal{E}}$ SLOW!



Approximate methods

$$\mathbf{I}^{\mathbf{A}}(t) = \mathrm{Tr}_{B} \Big[\exp_{+} \big[-i \big(\hat{H}_{S} t \big) + \int_{0}^{t} d\tau \big(\hat{H}_{SB}(\tau) \big) \big] \hat{\rho}_{B}^{\mathrm{eq}} \Big],$$

$$\langle e^{kt} \rangle_{B}$$



 $\langle \xi_n(t) \rangle = 0$ mean $\langle \xi_n(t) \xi_n(t') \rangle = C_n(t-t')$ variance

energy deviation

Approximate methods

energy deviation



Approximate methods

$$\mathbf{I}^{\mathbf{A}}(t) = \mathrm{Tr}_{B} \Big[\exp_{+} \big[-i \big(\hat{H}_{S} t \big) + \int_{0}^{t} d\tau \big(\hat{H}_{SB}(\tau) \big) \big] \hat{\rho}_{B}^{\mathrm{eq}} \Big],$$



$\langle e^{kt} \rangle_B$

Plan:

 $\langle \xi_n(t) \rangle = 0$ $\langle \xi_n(t) \xi_n(t') \rangle = C_n(t-t')$ variance

mean

Expand I^A(t) in cumulants of \hat{H}_{SB}

$$\mathbf{I}^{\mathbf{A}}(t) = e^{-\hat{H}_{S}t}e^{-K(t)}$$

Based on our conceptual model of the first lecture:

- light causes oscillations in the charges of the pigment molecules
- pigment molecules interact such that excitation (by light) of one causes excitation in some others (delocalization)
- the orientation of pigment molecules determine the extent of delocalization
- nuclear motion can cause energy transfer between eigenstates (the energy is transferred to nuclear vibrations)
- nuclear motions has the form of correlated random noise; the correlation function of the charge fluctuation gives information about the frequency of the charge fluctuation as well as the nuclear vibrations.





 $\mathcal{R}^{(3)}(\tau_3, \tau_2, \tau_1) = i^n \operatorname{Tr}[\hat{\mu} \mathcal{U}_{\mathrm{mol}}(\tau_3) \mathcal{V} \mathcal{U}_{\mathrm{mol}}(\tau_2) \mathcal{V} \mathcal{U}_{\mathrm{mol}}(\tau_1) \mathcal{V} \rho^{\mathrm{eq}}]$












Third-order response





Third-order response





Heterodyne detection





Heterodyne detection



$$I_{\text{det}} = |E_S + E_{\text{LO}}|^2 = |E_s|^2 + |E_{\text{LO}}|^2 + 2\text{Re}|E_S E_{\text{LO}}^*|$$

small known

Pump-probe spectroscopy $\Delta Abs = Abs_{pump \ on} - Abs_{pump \ off}$ Pump \bigcirc probe probe

$$\begin{split} \Delta Abs &= Abs_{pump \ on} - Abs_{pump \ off} \\ \Delta I &= I_{pump \ on} - I_{pump \ off} \end{split}$$





why is pump-probe a third-order technique?



equilibrium























Pump-probe spectroscopy with pump probe start pump les imp probe























