NITheCS mini-school

Modelling optical spectra

21 August

Towan Nöthling

Linear and nonlinear optical spectroscopy


End of route
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End of route
equations
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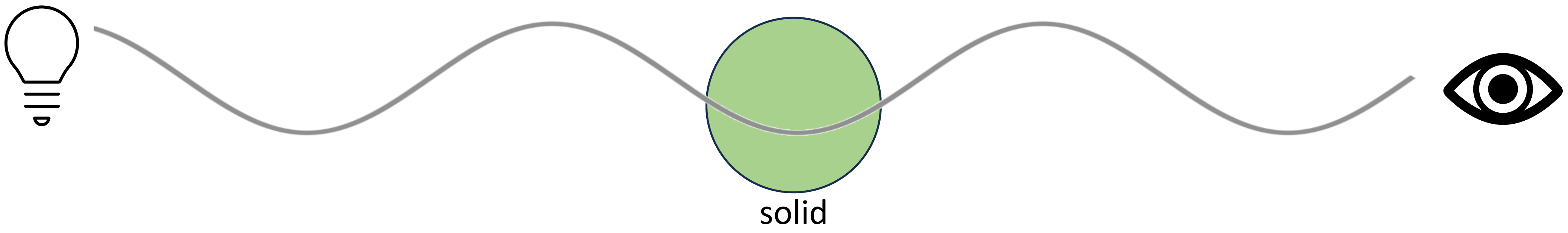
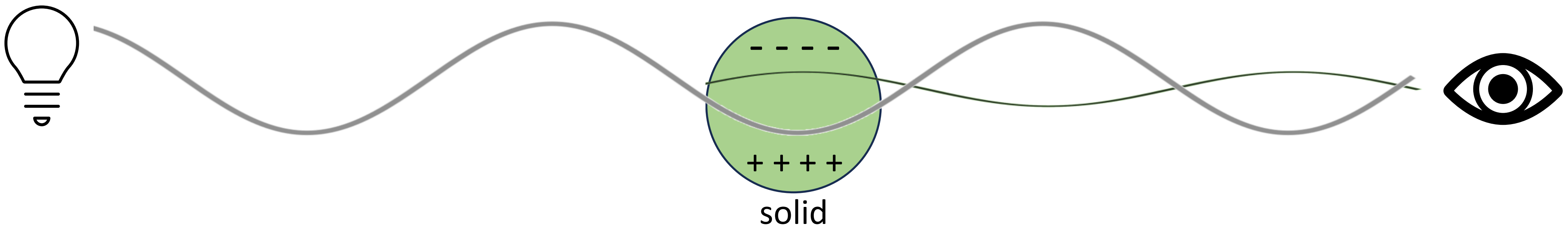
Aerial view

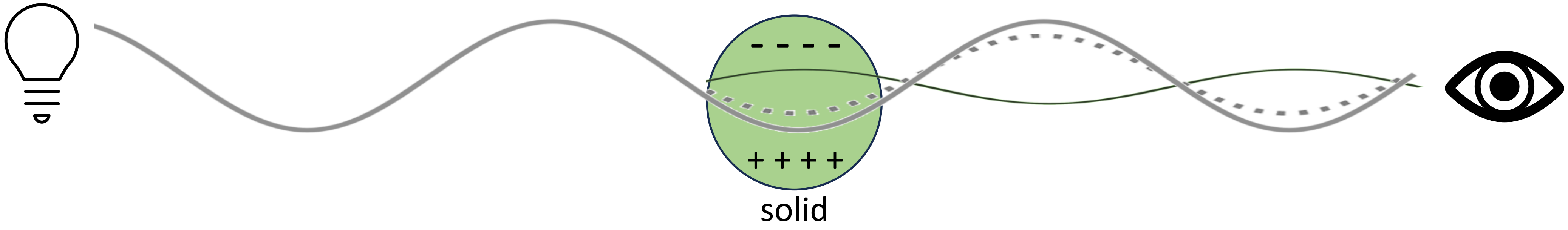
Aerial view



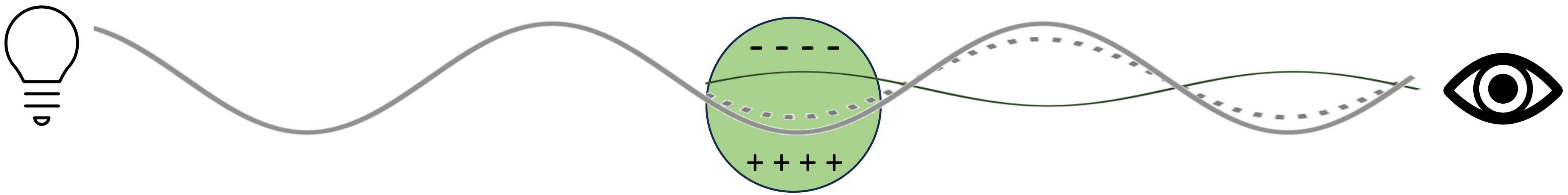
Aerial view



Aerial view



Aerial view



1. Maxwell's equations relate the induced polarization to the measured electric field.
2. The different orders of polarization relate to different orders of spectroscopy (linear and nonlinear).
3. Spectral signals can be calculated from the system response functions.

classical

4. The polarization depends on the quantum dynamics in the material.
5. Calculate linear response function.
6. Discuss an exact method for calculating linear spectra.
7. Calculating approximate spectra.

quantum mechanics

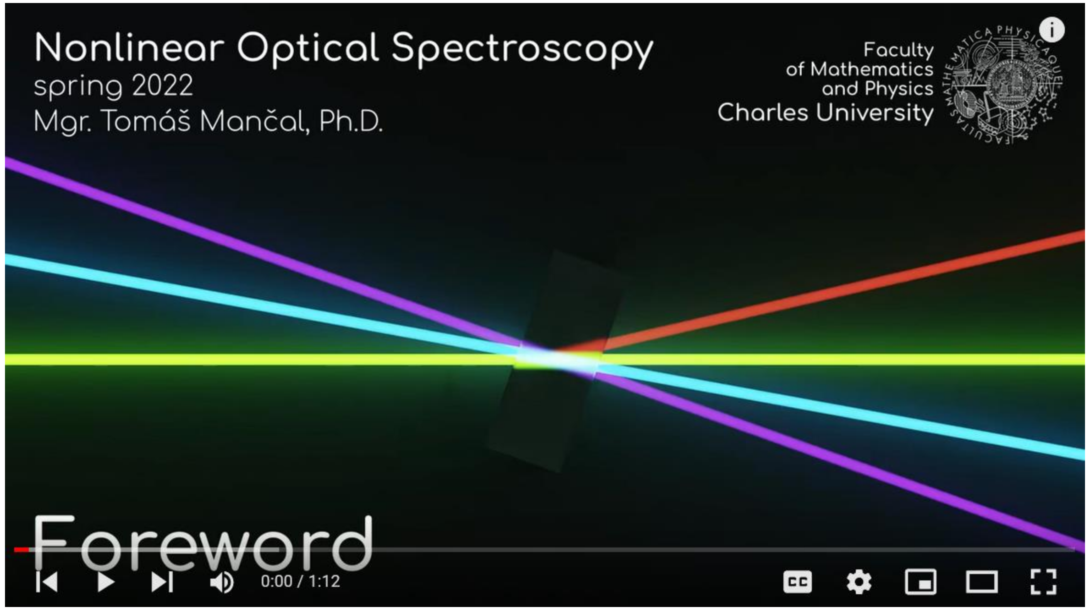
Electric field and polarization

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$ Gauss's law

$$\nabla \cdot \mathbf{B} = 0$$ No magnetic monopoles

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$ Faraday’s law of induction

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t}$$ Ampère's law



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

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

Electric field and polarization

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

$\downarrow$ Fourier transform

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

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

Linear polarization

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

Fourier transform

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Linear polarization

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

$$\Big\downarrow \text{ Fourier transform}$$

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

$$\left[-k^2 + \frac{\omega^2}{c^2}\left(1+\chi(\omega)\right)\right]\boldsymbol{E}^{\perp}(\omega) = 0$$

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

Linear polarization and absorption

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

Fourier transform

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

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

$$\underbrace{\left[-k^2 + \frac{\omega^2}{c^2}\left(1 + \chi(\omega)\right)\right]}_{=0} \boldsymbol{E}^{\perp}(\omega) = 0$$

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

Linear polarization and absorption

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

Fourier transform

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

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

$$\underbrace{\left[-k^2 + \frac{\omega^2}{c^2}(1 + \chi(\omega))\right]}_{=0} \boldsymbol{E}^{\perp}(\omega) = 0$$

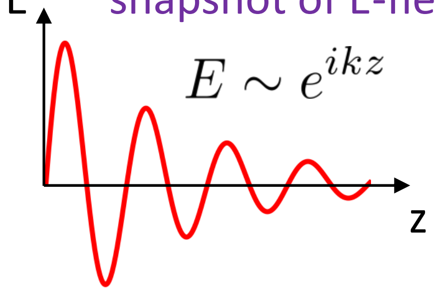
$$k = \frac{\omega}{c}\sqrt{1 + \chi(\omega)} \qquad \chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$

algebra

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

snapshot of E-field

$$E \sim e^{ikz}$$



$$I = I_0 e^{-\alpha(\omega) z}$$

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

Orders of polarization

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

susceptibilities

Orders of polarization

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

linear spectroscopy

Orders of polarization

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

nonlinear spectroscopy

Susceptibility

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

susceptibilities

$$P^{(n)} = P^{(n)}(\omega)$$
$$E = E(\omega)$$
$$\chi^{(n)} = \chi^{(n)}(\omega)$$

P In the time domain

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

susceptibilities

$$P^{(n)} = P^{(n)}(\omega)$$
$$E = E(\omega)$$
$$\chi^{(n)} = \chi^{(n)}(\omega)$$

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

Response functions

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

susceptibilities

$$P^{(n)} = P^{(n)}(\omega)$$
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$$P(t) = P^{(0)}(t) + P^{(1)}(t) + P^{(2)}(t) + \ldots$$

$$\boxed{P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \ldots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1)E(t-\tau_n)E(t-\tau_n-\tau_{n-1})\ldots E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)}$$

Response functions

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

susceptibilities

$$P^{(n)} = P^{(n)}(\omega)$$
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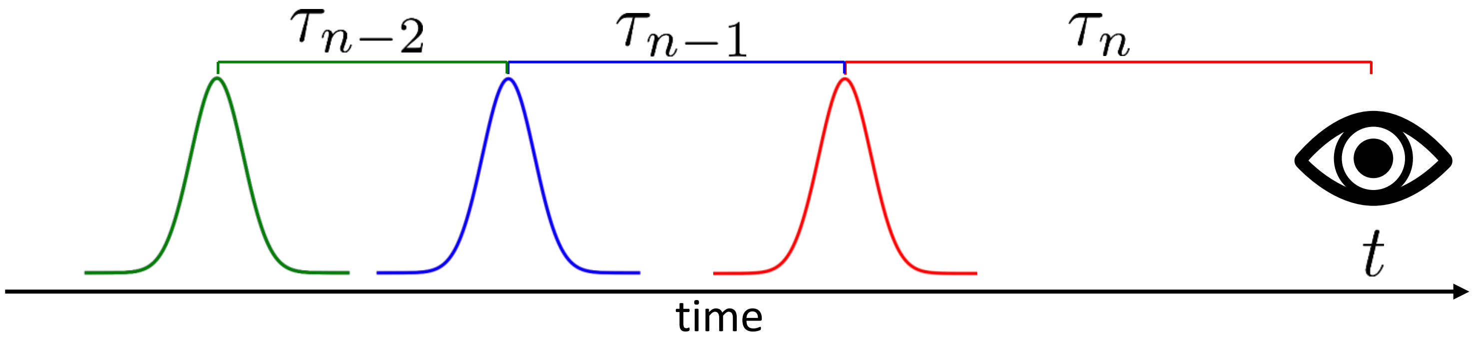

Response functions

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

susceptibilities

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

Summary

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

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

$$\boxed{\begin{aligned} P^{(n)} &= P^{(n)}(\omega) \\ E &= E(\omega) \\ \chi^{(n)} &= \chi^{(n)}(\omega) \end{aligned}}$$

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

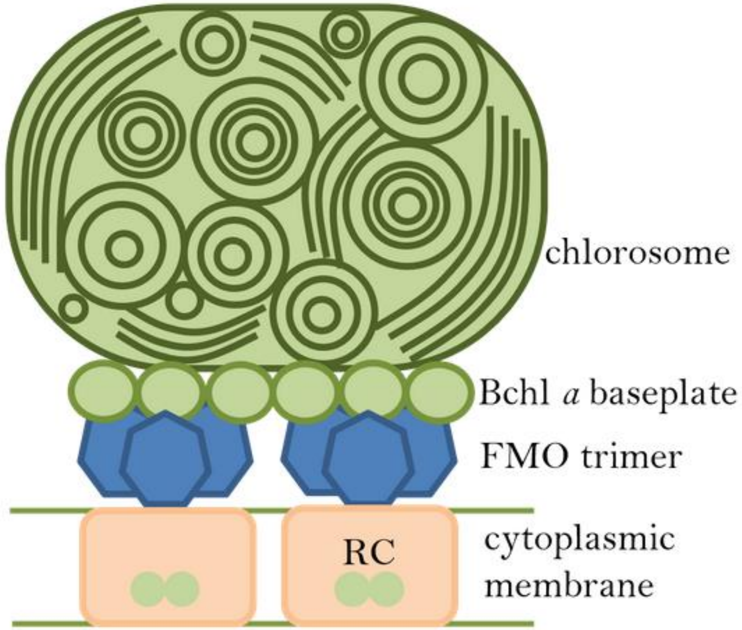
$$\boxed{\chi(\omega) = \chi'(\omega) + i\chi''(\omega)}$$

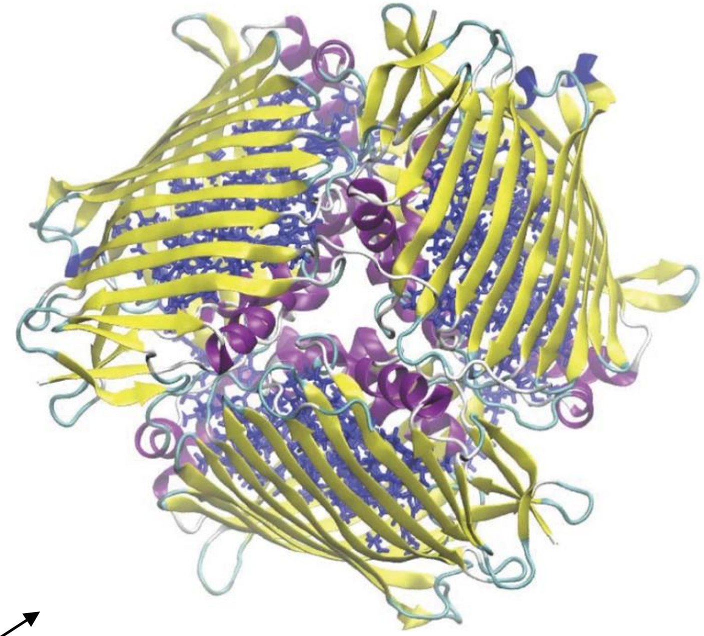
$$\boxed{P^{(n)}(t) = \int_0^{\infty} d\tau_n \int_0^{\infty} d\tau_{n-1} \ldots \int_0^{\infty} d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) E(t-\tau_n) E(t-\tau_n-\tau_{n-1}) \ldots E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)}$$

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

QM of linear response

FMO complex





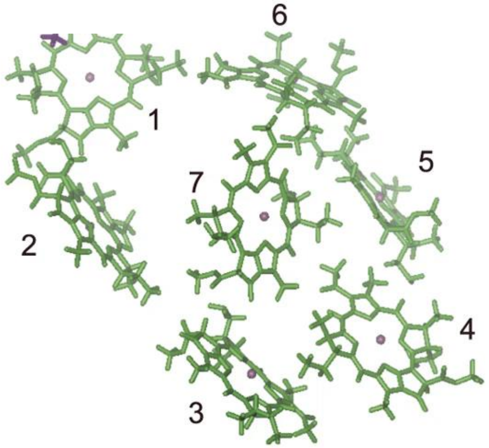
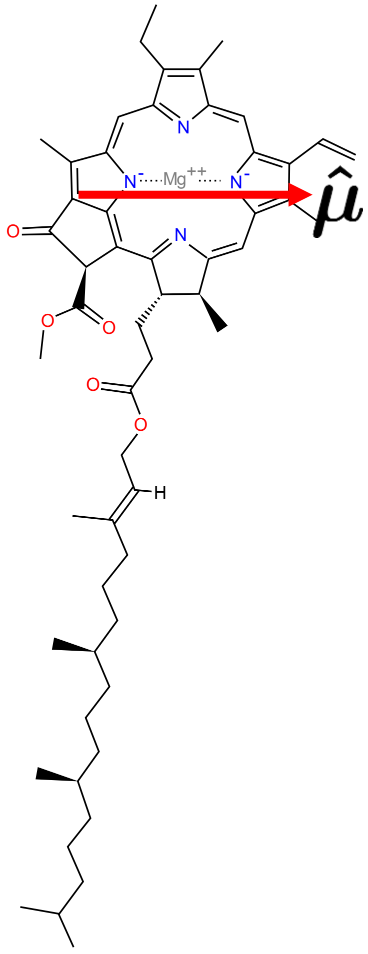


Figure credit: Jia, X., Mei, Y., Zhang, J. *et al*. *Sci Rep* **5**, 17096 (2015). CC BY 4.0

Quantum system: radiation-matter interaction

$$\hat{H}_{\text{rad-mat}}(t) = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

$$\hat{\boldsymbol{\mu}} = \sum_n \boldsymbol{\mu}_n \left(|n\rangle \langle g| + |g\rangle \langle n| \right)$$

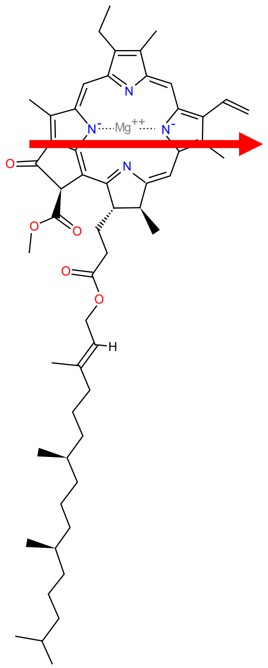


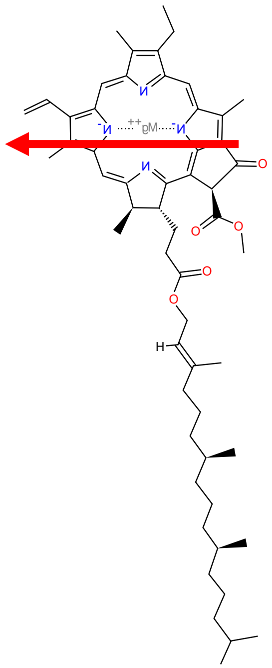
$|e\rangle$

$|g\rangle$

Quantum system: electronic H

$$\hat{H}_{\mathrm{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$





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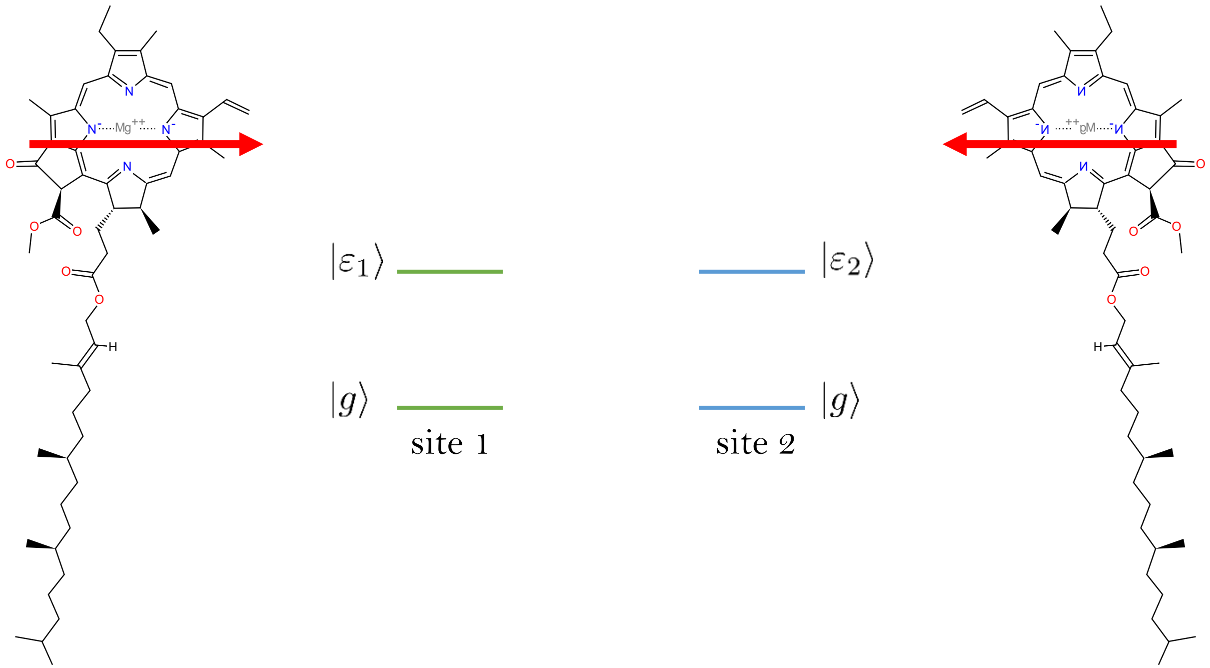
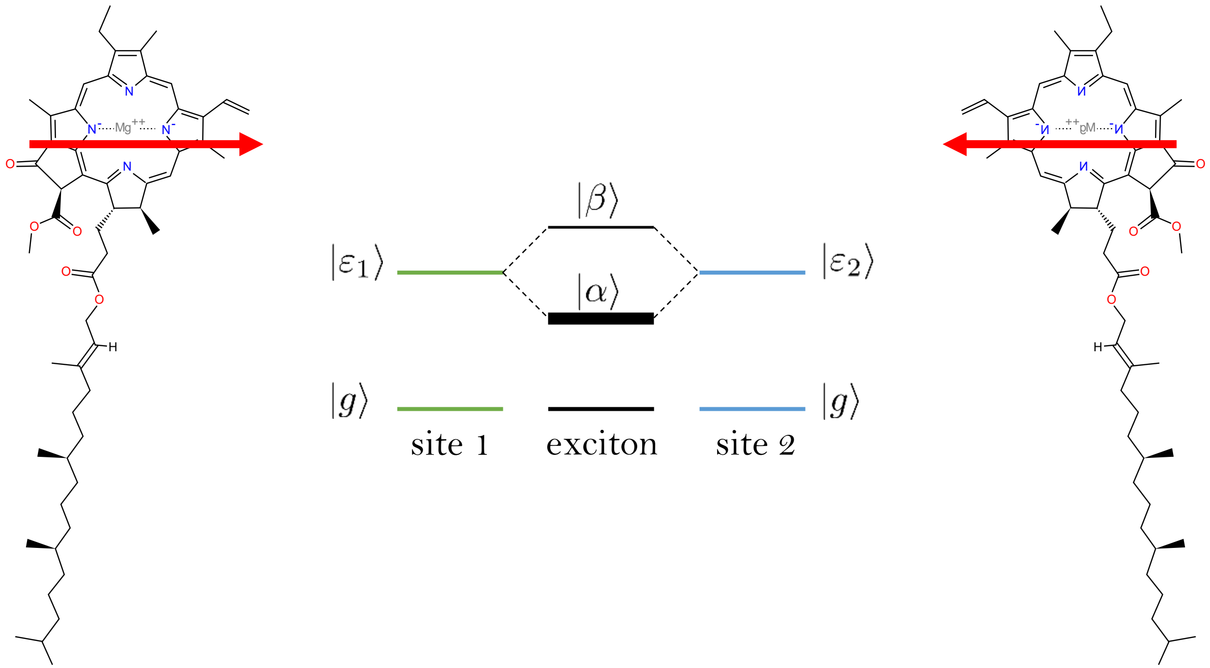


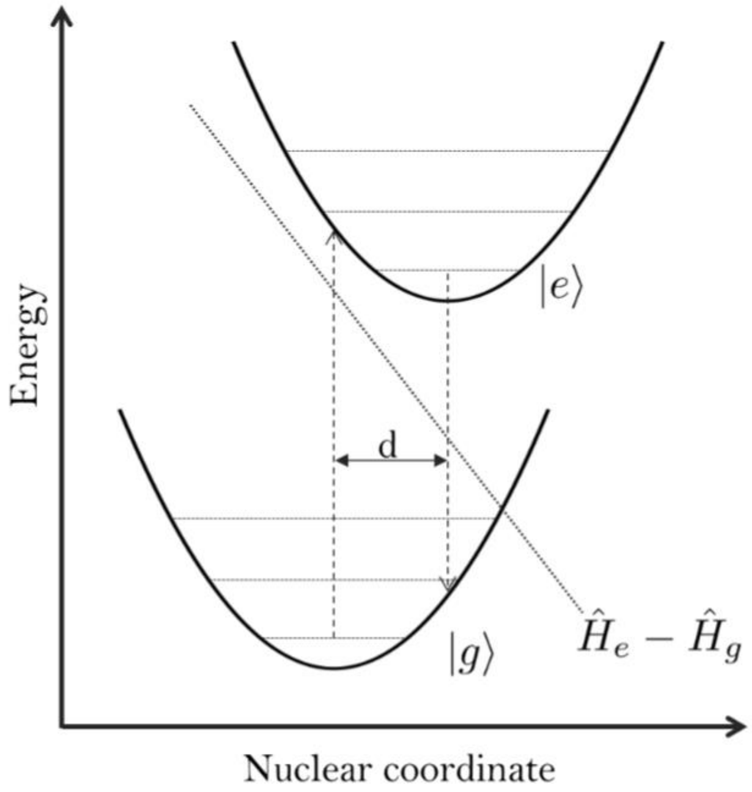
Quantum system: electronic H

$$\hat{H}_{\mathrm{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$



Quantum system: nuclear H

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



Full Hamiltonian

We have:

$$\hat{H}_{\text{rad-mat}}(t) = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

$$\hat{H}_{\text{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

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

Bath

Full Hamiltonian

We have:

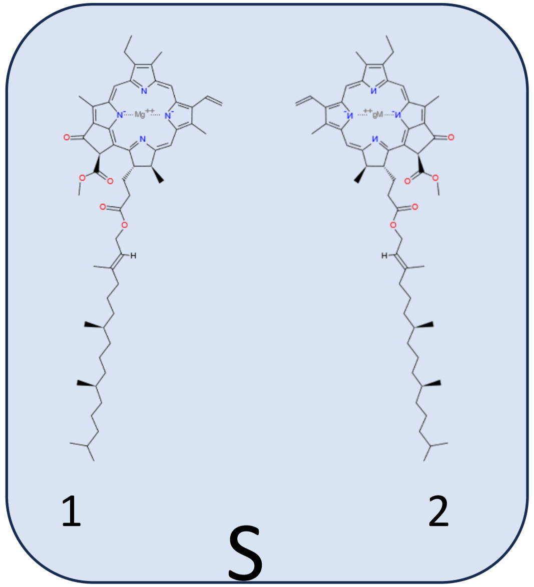
$$\hat{H}_{\text{rad-mat}}(t) = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

$$\hat{H}_{\text{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

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

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

Quantum Mechanics: density operator



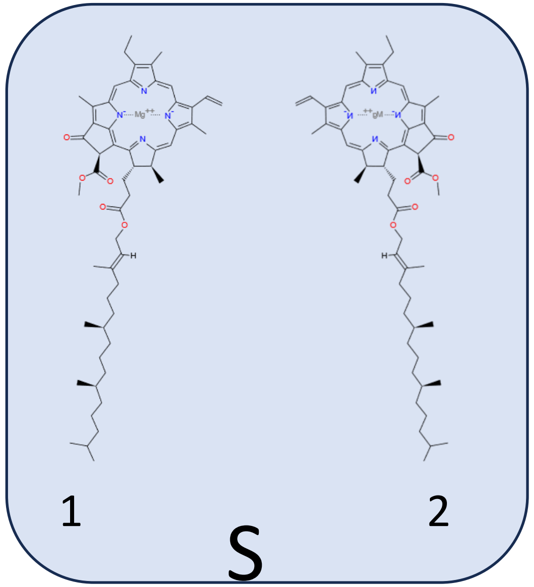
$$|\psi\rangle_S = \alpha\,|1\rangle + \beta\,|2\rangle$$

exciton (superposition) state

Only pigment 1 excited

Only pigment 2 excited

Quantum Mechanics: density operator



$$|\psi\rangle_S = \alpha\,|1\rangle + \beta\,|2\rangle$$

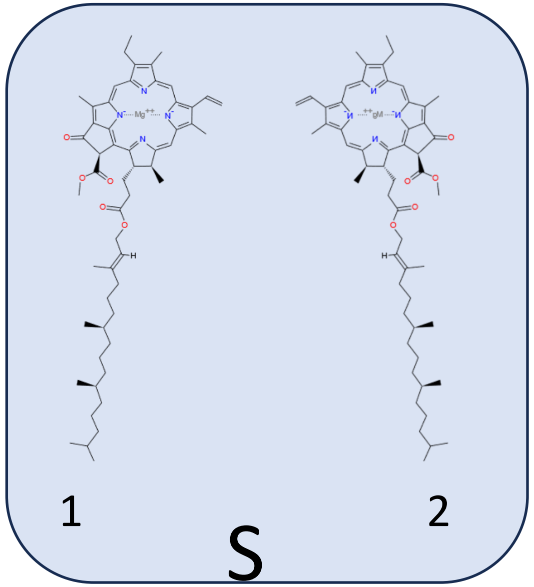
$$\hat{\rho}_S = |\psi\rangle_S\,\langle\psi|_S$$

coherences

$$\rho_S = \begin{bmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{bmatrix}$$

populations

Quantum Mechanics: density operator



$$|\psi\rangle_S = \alpha\,|1\rangle + \beta\,|2\rangle$$

$$\hat{\rho}_S = |\psi\rangle\,\langle\psi|$$

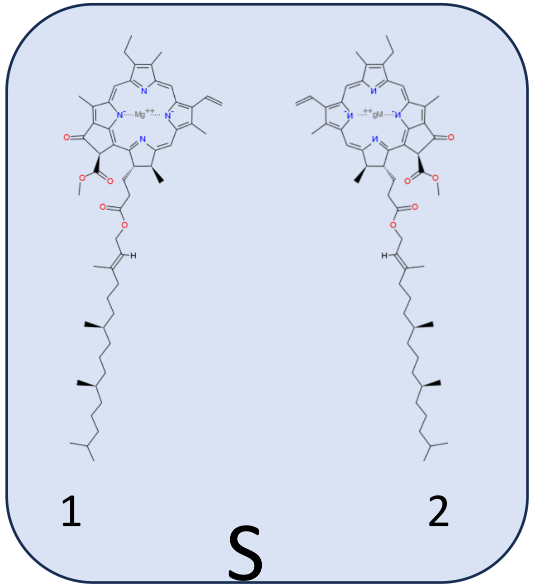
coherences

$$\rho_S = \begin{bmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{bmatrix}$$

populations

$$\mathrm{Tr}(\rho_S) = |\alpha|^2 + |\beta|^2$$

Quantum Mechanics: density operator



$$|\psi\rangle_S = \alpha\,|1\rangle + \beta\,|2\rangle$$

$$\hat{\rho}_S = |\psi\rangle\,\langle\psi|$$

coherences

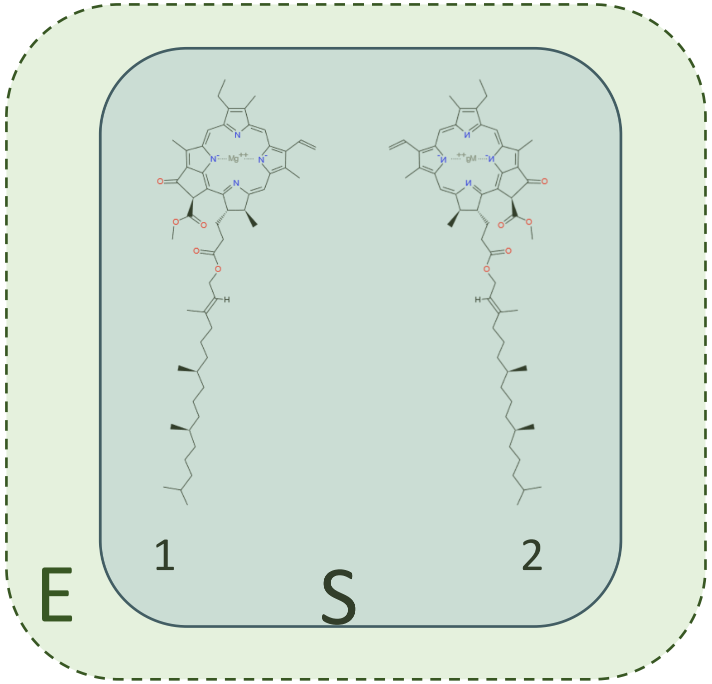
$$\rho_S = \begin{bmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{bmatrix}$$

populations

$$\mathrm{Tr}(\rho_S) = |\alpha|^2 + |\beta|^2$$

$$\langle\hat{A}\rangle = \mathrm{Tr}(\hat{A}\hat{\rho}_S)$$

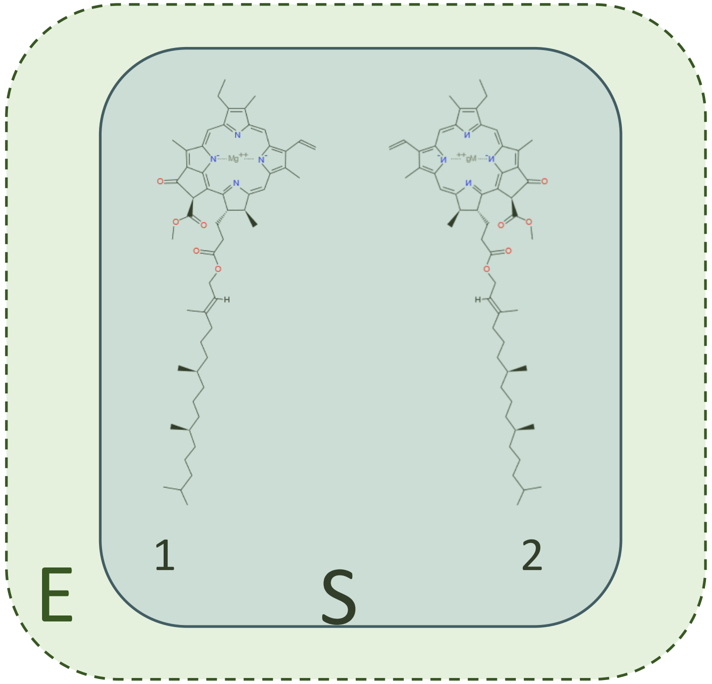
Quantum Mechanics: density operator



$$|\Psi\rangle = \alpha\,|1\rangle\,|E_1\rangle + \beta\,|2\rangle\,|E_2\rangle$$

$$\hat{\rho} = |\Psi\rangle\,\langle\Psi|$$

Quantum Mechanics: density operator



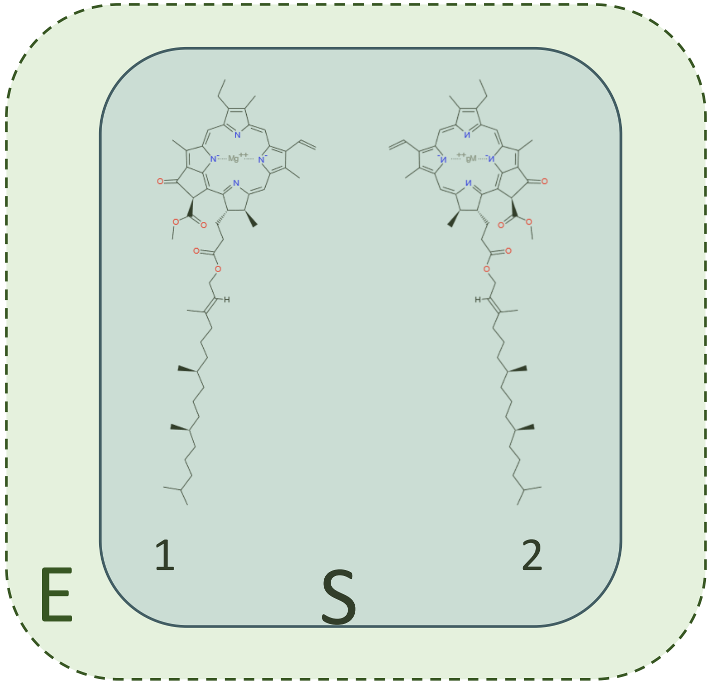
$$|\Psi\rangle = \alpha\,|1\rangle\,|\mathrm{E}_1\rangle + \beta\,|2\rangle\,|\mathrm{E}_2\rangle$$

$$\hat{\rho} = |\Psi\rangle\,\langle\Psi|$$

$$\mathrm{Tr}_E(\rho)$$

$$\langle\hat{A}\rangle_E = \mathrm{Tr}_E(\hat{A}\hat{\rho})$$

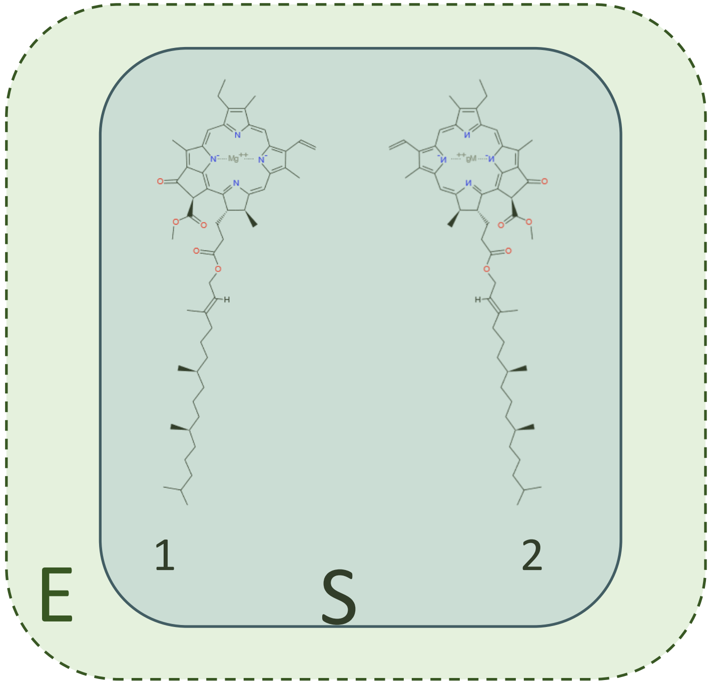
Quantum Mechanics: equilibrium density operator



At equilibrium:

$$\hat{\rho}^{\mathrm{eq}}$$

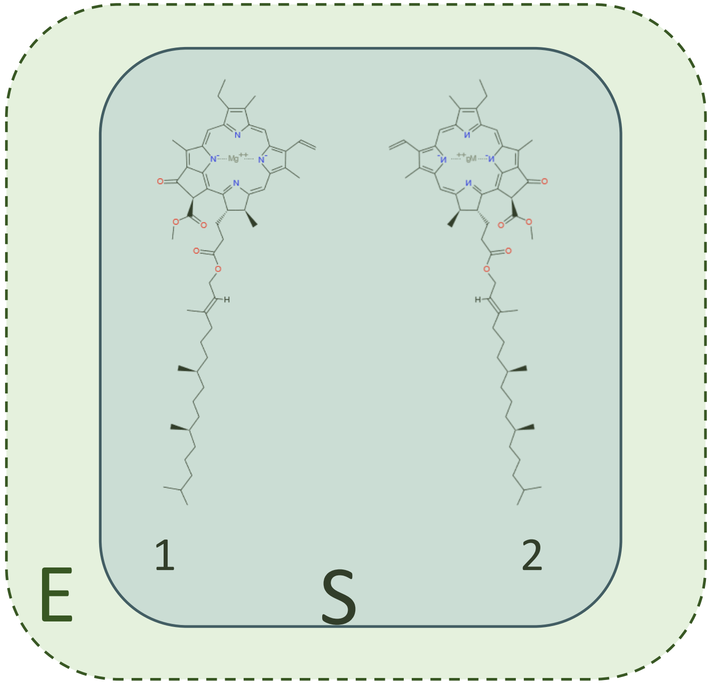
Quantum Mechanics: superoperators



$$\hat{\rho} = |\Psi\rangle \langle\Psi|$$

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

Quantum Mechanics: superoperators



$$\hat{\rho} = |\Psi\rangle \langle\Psi|$$

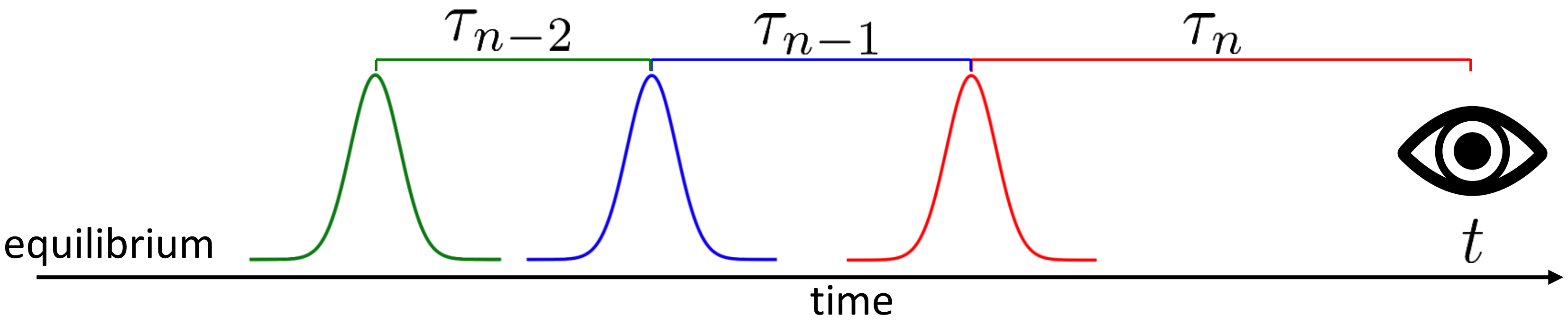
$$\hat{\rho}(t) = \hat{U}(t) |\Psi\rangle \langle\Psi| \hat{U}^\dagger(t)$$
$$= \mathcal{U}(t)\hat{\rho}(0)$$

Superoperators

$$\mathcal{V}\hat{A} = [\hat{\mu}, \hat{A}]$$

QM of response

$$P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \ldots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) \boxed{E(t-\tau_n)} \boxed{E(t-\tau_n-\tau_{n-1})} \ldots \boxed{E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)}$$

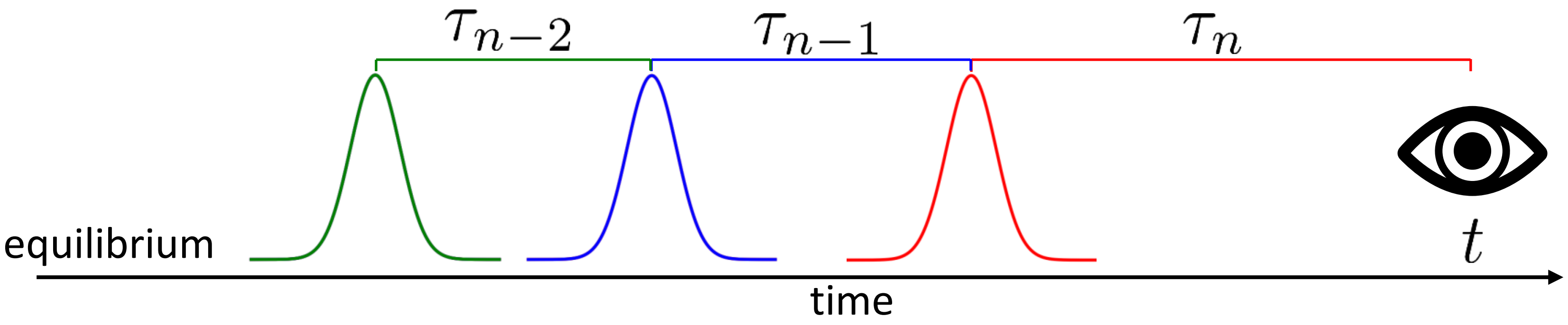


$$\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) = i^n \mathrm{Tr}[\hat{\mu}\,\mathcal{U}_{\mathrm{mol}}(\tau_n)\mathcal{V}\,\mathcal{U}_{\mathrm{mol}}(\tau_{n-1})\mathcal{V} \ldots \mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

$$\mathcal{V}\bullet = [\hat{\mu}, \bullet]$$

QM of response

$$P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \dots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \dots, \tau_1) \boxed{E(t-\tau_n)}\boxed{E(t-\tau_n-\tau_{n-1})} \dots \boxed{E(t-\tau_n-\tau_{n-1}-\dots-\tau_1)}$$

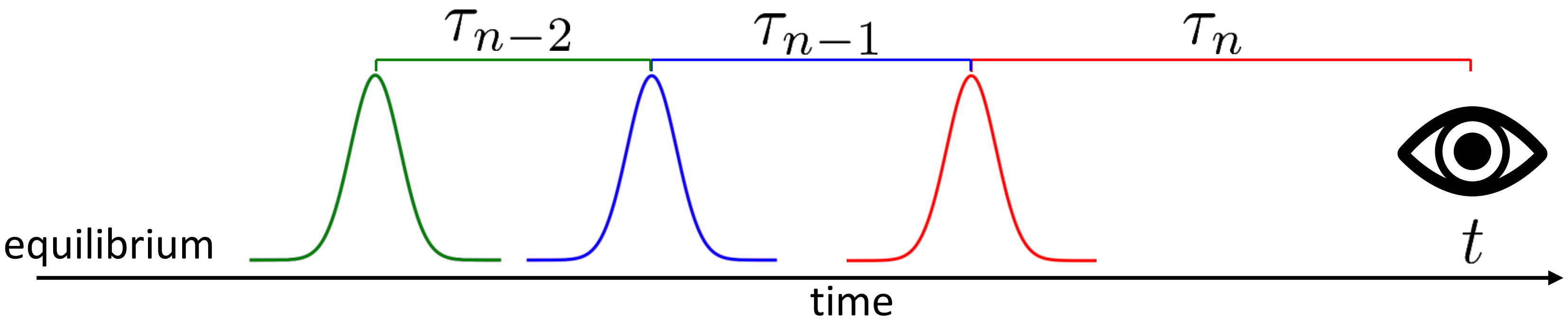


$$\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \dots, \tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_n)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_{n-1})\mathcal{V}\dots\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]$$

Evolution only under $\mathcal{U}_{\mathrm{mol}}$

QM of linear response

$$\boxed{P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \ldots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) \boxed{E(t-\tau_n)} \boxed{E(t-\tau_n-\tau_{n-1})} \ldots \boxed{E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)}}$$



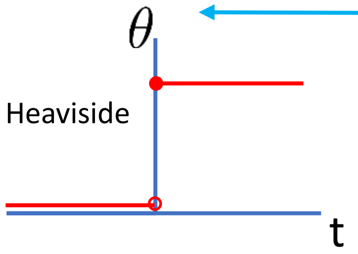
$$\boxed{\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_n)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_{n-1})\mathcal{V}\ldots\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]}$$

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

Back to linear response

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

$$= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)]$$

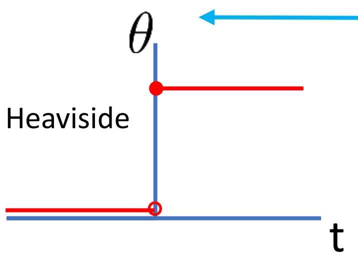


linear response function

Back to linear response

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

$$= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)]$$

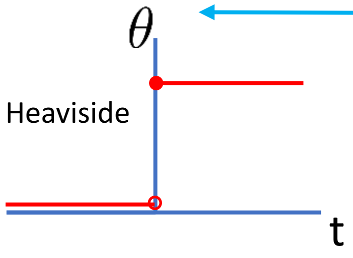


$$R^{(1)}(t) = \mathrm{Tr}[e^{i\hat{H}_{\mathrm{mol}}t}\hat{\boldsymbol{\mu}}e^{-i\hat{H}_{\mathrm{mol}}t}\hat{\boldsymbol{\mu}}\hat{\rho}^{\mathrm{eq}}] = \langle\hat{\mu}(t)\hat{\mu}(0)\rangle$$

Back to linear response

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

$$= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)]$$



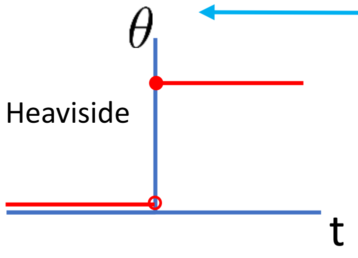
$$R^{(1)}(t) = \mathrm{Tr}[e^{i\hat{H}_{\mathrm{mol}}t}\hat{\boldsymbol{\mu}}e^{-i\hat{H}_{\mathrm{mol}}t}\hat{\boldsymbol{\mu}}\hat{\rho}^{\mathrm{eq}}] = \langle\hat{\mu}(t)\hat{\mu}(0)\rangle$$

fluctuation of dipole

Back to linear response

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

$$= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)]$$



assume $\hat{\rho}^{\mathrm{eq}} = |g\rangle\langle g|\,\hat{\rho}_B^{\mathrm{eq}}$

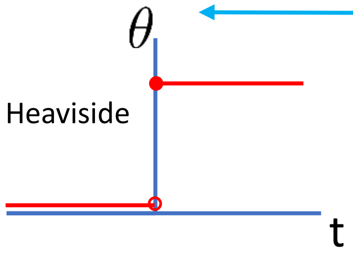
(for absorption)

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

Back to linear response

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

$$= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)]$$



assume $\hat{\rho}^{\mathrm{eq}} = |g\rangle\langle g|\,\hat{\rho}_B^{\mathrm{eq}}$

(for absorption)

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

$$= \sum_{m=1}^{N}\sum_{n=1}^{N}\boldsymbol{\mu}_m\cdot\boldsymbol{\mu}_n\mathrm{Tr}_B[\langle g|\,e^{i\hat{H}_{\mathrm{mol}}t}\,|g\rangle \times \langle m|\,e^{-i\hat{H}_{\mathrm{mol}}t}\,|n\rangle\,\hat{\rho}_B^{\mathrm{eq}}]$$

$$= \sum_m\sum_n\boldsymbol{\mu}_m\cdot\boldsymbol{\mu}_n\,\langle n|\,\mathrm{Tr}_B[e^{-i\hat{H}_g t}e^{i\hat{H}_e t}\hat{\rho}^{\mathrm{eq}}]\,|m\rangle$$

$$= \sum_m\sum_n\boldsymbol{\mu}_m\cdot\boldsymbol{\mu}_n\,\mathrm{I}_{mn}$$

Absorption spectrum

$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto 2\mathrm{Re}\int_0^\infty dt\, e^{i\omega t} R^{(1)}(t)}$$

Absorption spectrum

$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto 2\mathrm{Re} \int_0^{\infty} dt\, e^{i\omega t} R^{(1)}(t)}$$

$$R^{(1)}(t) = \sum_m \sum_n \boldsymbol{\mu}_m \cdot \boldsymbol{\mu}_n \, \mathrm{I}_{mn}$$

$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[2\mathrm{Re} \int_0^{\infty} dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]}$$

Dipole factor matrix

Spectral tensor

Absorption and emission spectra

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

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

Summary

$$\boxed{P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \ldots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) E(t-\tau_n) E(t-\tau_n-\tau_{n-1}) \ldots E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)}$$

$$\boxed{\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) = i^n \mathrm{Tr}[\hat{\mu} \mathcal{U}_{\mathrm{mol}}(\tau_n) \mathcal{V} \mathcal{U}_{\mathrm{mol}}(\tau_{n-1}) \mathcal{V} \ldots \mathcal{U}_{\mathrm{mol}}(\tau_1) \mathcal{V} \rho^{\mathrm{eq}}]}$$

$$\boxed{\begin{aligned} \mathcal{R}^{(1)}(t) &= i\mathrm{Tr}[\hat{\mu} \mathcal{U}_{\mathrm{mol}}(t) \mathcal{V} \rho^{\mathrm{eq}}] \\ &= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)] \end{aligned}}$$

$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto 2\mathrm{Re} \int_0^\infty dt\, e^{i\omega t} R^{(1)}(t)}$$

$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[2\mathrm{Re} \int_0^\infty dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]}$$

$$\boxed{\mathrm{S}^{\mathrm{E}}(\omega) \propto \omega^3 \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{E}} \left[2\mathrm{Re} \int_0^\infty dt\, e^{-i\omega t} \mathrm{I}_{mn}^{\mathrm{E}}(t) \right]}$$

Summary

$$\boxed{P^{(n)}(t) = \int_0^\infty d\tau_n \int_0^\infty d\tau_{n-1} \ldots \int_0^\infty d\tau_1 \mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) E(t-\tau_n) E(t-\tau_n-\tau_{n-1}) \ldots E(t-\tau_n-\tau_{n-1}-\ldots-\tau_1)}$$

$$\boxed{\mathcal{R}^{(n)}(\tau_n, \tau_{n-1}, \ldots, \tau_1) = i^n \mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(\tau_n)\mathcal{V}\mathcal{U}_{\mathrm{mol}}(\tau_{n-1})\mathcal{V}\ldots\mathcal{U}_{\mathrm{mol}}(\tau_1)\mathcal{V}\rho^{\mathrm{eq}}]}$$

$$\boxed{\begin{aligned}\mathcal{R}^{(1)}(t) &= i\mathrm{Tr}[\hat{\mu}\mathcal{U}_{\mathrm{mol}}(t)\mathcal{V}\rho^{\mathrm{eq}}] \\ &= i\theta(t)[R^{(1)}(t) - R^{(1)*}(t)]\end{aligned}}$$

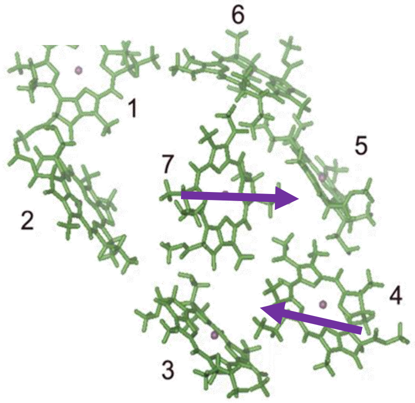
$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto 2\mathrm{Re} \int_0^\infty dt\, e^{i\omega t} R^{(1)}(t)}$$

$$\boxed{\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[2\mathrm{Re} \int_0^\infty dt\, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t)\right]}$$

$$\boxed{\mathrm{S}^{\mathrm{E}}(\omega) \propto \omega^3 \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{E}} \left[2\mathrm{Re} \int_0^\infty dt\, e^{-i\omega t} \mathrm{I}_{mn}^{\mathrm{E}}(t)\right]}$$

Absorption spectroscopy

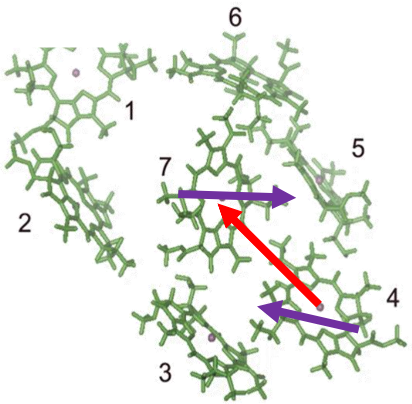
$$\mathrm{S}^{\mathrm{A}}(\omega) \propto \omega \sum_{m=1}^{N} \sum_{n=1}^{N} f_{mn}^{\mu,\mathrm{A}} \left[2\mathrm{Re} \int_{0}^{\infty} dt \, e^{i\omega t} \mathrm{I}_{mn}^{\mathrm{A}}(t) \right]$$

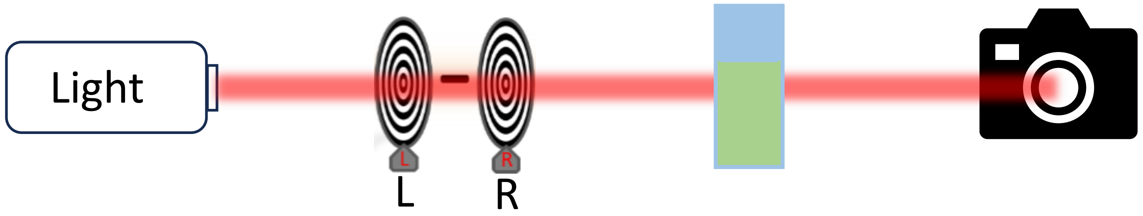


$$f_{mn}^{\mu,\mathrm{A}} = \boldsymbol{\mu}_m \cdot \boldsymbol{\mu}_n$$

Circular dichroism spectroscopy

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

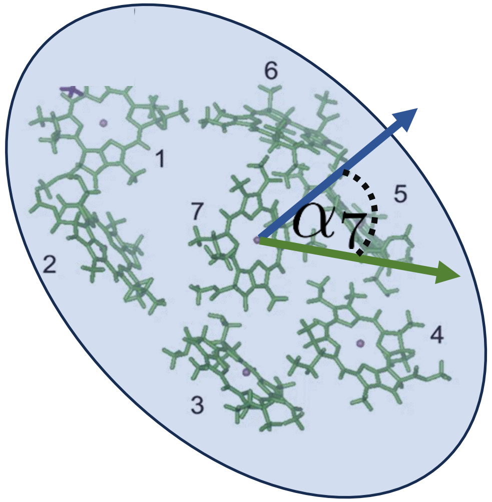


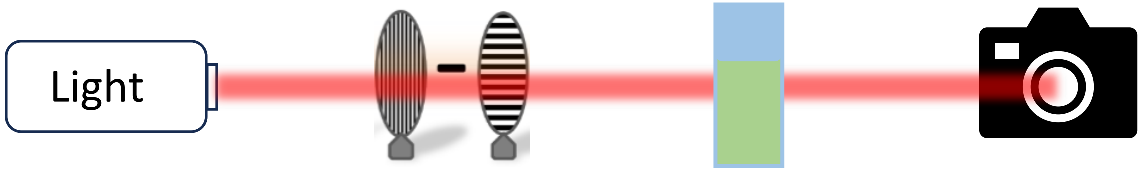


$$f_{mn}^{\mu,\mathrm{CD}} = \sqrt{\varepsilon_m \varepsilon_n}\,\boxed{(\boldsymbol{R}_m - \boldsymbol{R}_n)} \cdot \boxed{(\boldsymbol{\mu}_m \times \boldsymbol{\mu}_n)}$$

Linear dichroism spectroscopy

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





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

Spectral tensor

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

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

??

Spectral tensor

$$\hat{H}_{\text{rad-mat}}(t) = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

$$\hat{H}_{\text{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

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

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

Spectral tensor

$$\hat{H}_{\text{rad-mat}}(t) = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

$$\hat{H}_{\text{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m \neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

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

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

Let's define:

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

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

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

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

Spectral tensor

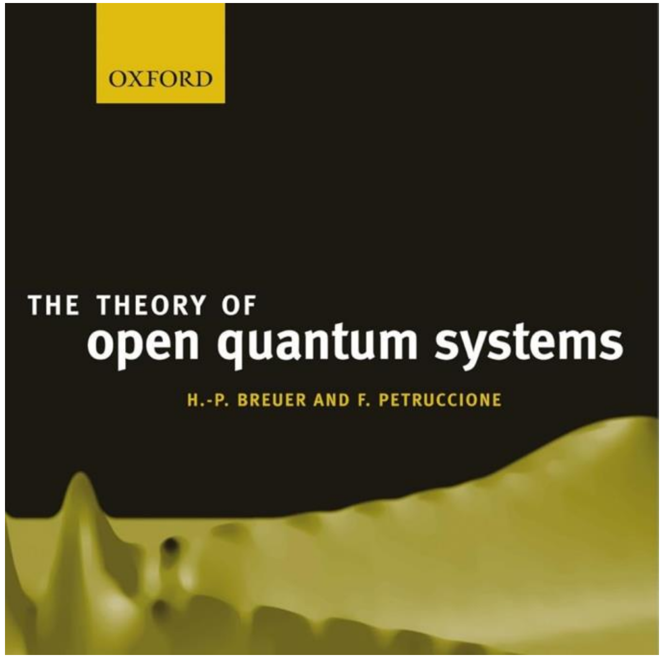
$$\hat{H}_{\text{rad-mat}}(t) = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(t)$$

$$\hat{H}_{\text{el}} = \sum_{n=1}^{N} \varepsilon_n \left|n\right\rangle \left\langle n\right| + \sum_{n=1}^{N} \sum_{\substack{m=1 \\ m\neq n}}^{N} J_{mn} \left|m\right\rangle \left\langle n\right| ,$$

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

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

Open quantum systems



Let's define:

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

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

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

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

Spectral tensor

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

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

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

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

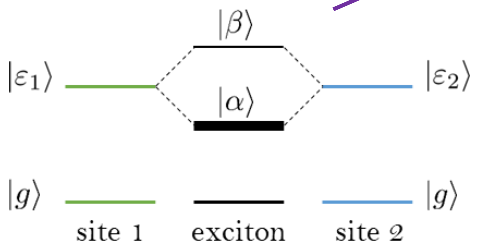
$$I = \mathrm{Tr}_B[e^{-i\hat{H}_{\mathrm{g}}t} e^{i\hat{H}_e t} \hat{\rho}^{\mathrm{eq}}]$$

$$\Big\downarrow \text{ algebra}$$

$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right] \hat{\rho}_B^{\mathrm{eq}}\right],}$$

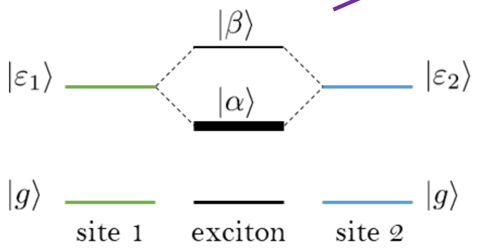
Spectral tensor

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B \left[\exp_+ \left[-i \left(\hat{H}_S t + \int_0^t d\tau \, \hat{H}_{SB}(\tau) \right) \right] \hat{\rho}_B^{\mathrm{eq}} \right],$$

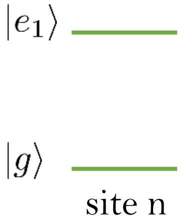


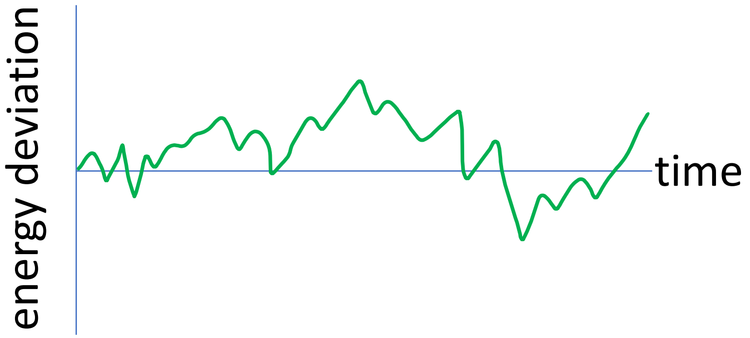
Spectral tensor

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$



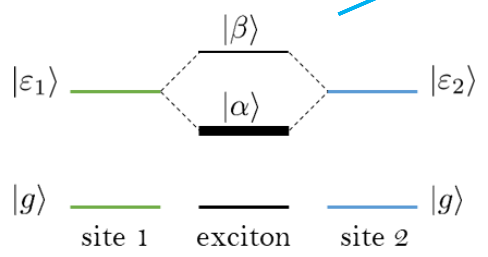
Interaction with huge number of vibrations in protein.



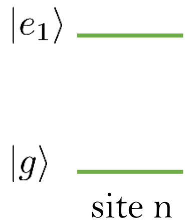


Spectral tensor

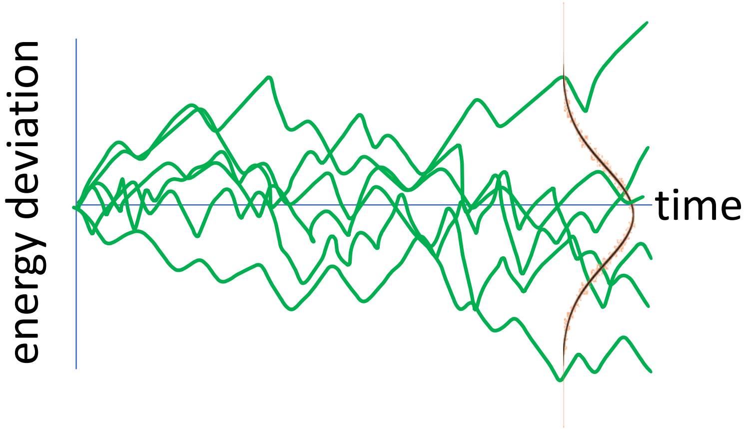
$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],}$$



Interaction with huge number of vibrations in protein.



$$\begin{aligned}
\langle \xi_n(t) \rangle &= 0 \\
\langle \xi_n(t)\xi_n(t') \rangle &= C_n(t-t') \\
\langle \xi_n(t)\xi_m(t') \rangle &= 0
\end{aligned}$$



Exact method

$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],}$$

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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

Citation: The Journal of Chemical Physics **142**, 094108 (2015); doi: 10.1063/1.4908601
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Exact method

$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\Big[\exp_+\big[-i\big(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\big)\big]\,\hat{\rho}_B^{\mathrm{eq}}\Big],}$$

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B(e^{kt}\hat{\rho}_B^{\mathrm{eq}})$$

$$= \langle e^{kt}\rangle_B$$

Exact method

$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\underbrace{\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]}\hat{\rho}_B^{\mathrm{eq}}\right],}$$

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B(e^{\overbrace{kt}}\hat{\rho}_B^{\mathrm{eq}})$$

$$= \langle e^{kt}\rangle_B$$

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

Exact method

$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],}$$

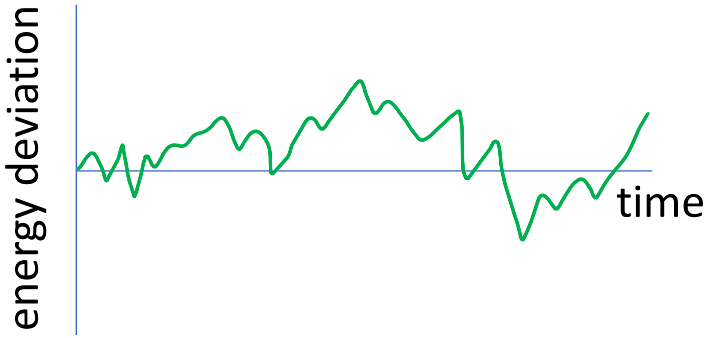
$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B(e^{kt}\hat{\rho}_B^{\mathrm{eq}})$$

$$= \langle e^{kt}\rangle_B$$

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

$$\frac{d}{dt}\mathcal{I}^{\mathrm{A}}(t) = -i\left(\hat{H}_S + \sum_{n=1}^{\infty} \xi_n(t)\,|n\rangle\,\langle n|\right)\mathcal{I}^{\mathrm{A}}(t)$$

$$\mathrm{I}^{\mathrm{A}}(t) = \langle \mathcal{I}^{\mathrm{A}}(t)\rangle_\xi$$



Exact method

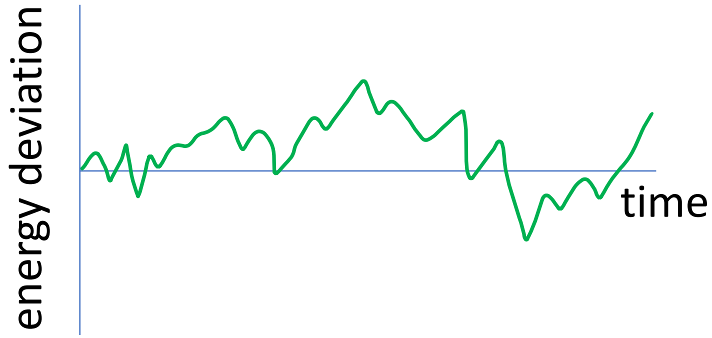
$$\boxed{\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\Big[\exp_+\big[-i\big(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\big)\big]\hat{\rho}_B^{\mathrm{eq}}\Big],}$$

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B(e^{kt}\hat{\rho}_B^{\mathrm{eq}}) = \langle e^{kt}\rangle_B$$

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

$$\frac{d}{dt}\mathcal{I}^{\mathrm{A}}(t) = -i\Big(\hat{H}_S + \sum_{n=1}^{\infty} \xi_n(t)\,|n\rangle\langle n|\Big)\mathcal{I}^{\mathrm{A}}(t)$$

$$\mathrm{I}^{\mathrm{A}}(t) = \langle \mathcal{I}^{\mathrm{A}}(t)\rangle_\xi$$

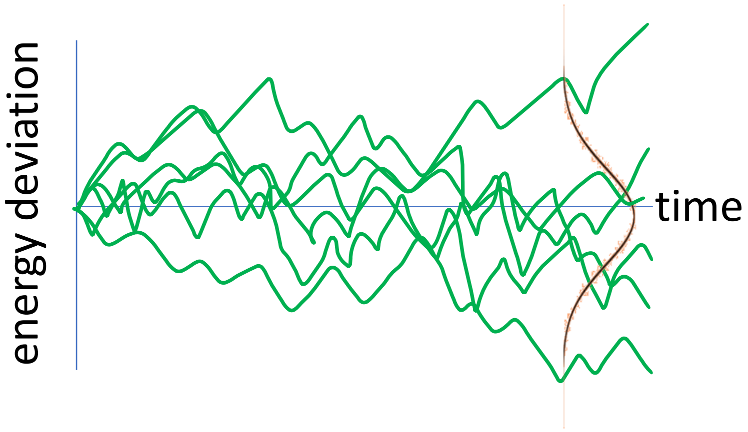


SLOW!

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$

$$\langle e^{kt} \rangle_B$$



$$\begin{aligned} \langle \xi_n(t) \rangle &= 0 \\ \langle \xi_n(t)\xi_n(t') \rangle &= C_n(t-t') \end{aligned}$$

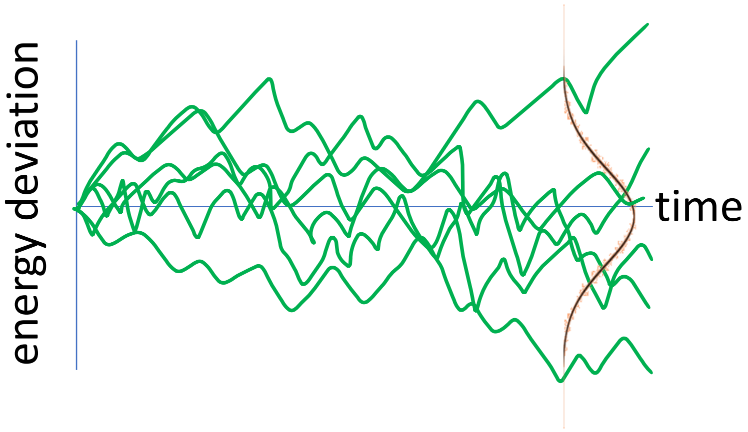
mean

variance

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$

$$\langle e^{kt}\rangle_B$$



Plan:

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

$$\begin{aligned} \langle \xi_n(t)\rangle &= 0 \\ \langle \xi_n(t)\xi_n(t')\rangle &= C_n(t-t') \end{aligned}$$

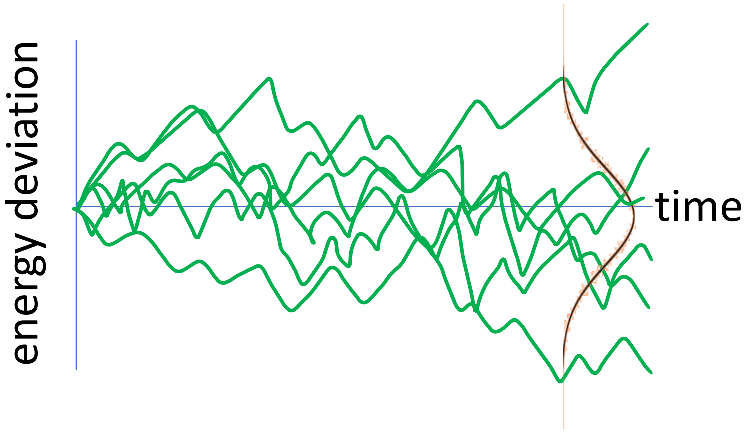
mean

variance

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$

$$\langle e^{kt}\rangle_B$$



$$\begin{aligned} \langle \xi_n(t)\rangle &= 0 && \text{mean} \\ \langle \xi_n(t)\xi_n(t')\rangle &= C_n(t-t') && \text{variance} \end{aligned}$$

Plan:

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

$$\mathrm{I}^{\mathrm{A}}(t) = e^{-i\hat{H}_S t} e^{-K(t)}$$

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$

Full Cumulant expansion (FCE)

Calculation time: ●●●○○ Accuracy: ●●●●○

$$\mathrm{I}^{\mathrm{A}}(t) = e^{-iH_S t} e^{-K(t)}$$

with

$$K_{\alpha\beta}(t) = \sum_{\delta=1}^{N} \int_0^t d\tau \int_0^\tau d\tau'\, e^{i\omega_{\alpha\delta}\tau - i\omega_{\beta\delta}\tau'} \times C_{\alpha\delta\delta\beta}(\tau-\tau').$$

Ma *et al. 2015.* J. Chem. Phys. 142(9) II

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$

Complex time-dependent Redfield (ctR)

Calculation time: ●●○○○ Accuracy: ●●●○○

$$\mathrm{I}^{\mathrm{A}}_{\alpha\beta}(t) = \delta_{\alpha\beta} e^{-i\varepsilon_\alpha t - g_{\alpha\alpha\alpha\alpha}(t) - \xi_\alpha(t)},$$

with

$$g_{\alpha\alpha\alpha\alpha}(t) = \int_0^t d\tau \int_0^\tau d\tau'\, C_{\alpha\alpha\alpha\alpha}(\tau')$$

and

$$\xi_\alpha(t) = \sum_{\beta\neq\alpha}^{N} \int_0^t d\tau \int_0^\tau d\tau'\, e^{i\omega_{\alpha\beta}\tau'} C_{\alpha\beta\beta\alpha}(\tau')$$

Gelzinis *et al*. 2015. J. Chem. Phys. 142(15)

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\Big[\exp_+\big[-i\big(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\big)\big]\hat{\rho}_B^{\mathrm{eq}}\Big],$$

Modified Redfield

Calculation time:

Accuracy:

$$\mathrm{I}^{\mathrm{A}}_{\alpha\beta}(t) = \delta_{\alpha\beta} e^{-i\varepsilon_\alpha t - g_{\alpha\alpha\alpha\alpha}(t) - R_\alpha(t)},$$

with

$$\begin{aligned} R_\alpha^{\mathrm{mR}} = & \sum_\beta \mathrm{Re} \int_0^\infty dt\, e^{i\omega_{\alpha\beta} t} \\ & \times \exp\Big(-g_{\beta\beta\beta\beta}(t) - g_{\alpha\alpha\alpha\alpha}(t) + g_{\alpha\alpha\beta\beta}(t) \\ & + g_{\beta\beta\alpha\alpha}(t) - 2i(\lambda_{\alpha\alpha\alpha\alpha} - \lambda_{\beta\beta\alpha\alpha})t\Big) \\ & \times \Big(C_{\beta\alpha\alpha\beta}(t) - [\dot{g}_{\alpha\beta\beta\beta}(t) - \dot{g}_{\alpha\beta\alpha\alpha}(t) - 2i\lambda_{\alpha\beta\alpha\alpha}] \\ & \times [\dot{g}_{\beta\beta\beta\alpha}(t) - \dot{g}_{\alpha\alpha\beta\alpha}(t) - 2i\lambda_{\beta\alpha\alpha\alpha}]\Big) \end{aligned}$$

Gelzinis *et al*. 2015. J. Chem. Phys. 142(15)

Approximate methods

$$\mathrm{I}^{\mathrm{A}}(t) = \mathrm{Tr}_B\left[\exp_+\left[-i\left(\hat{H}_S t + \int_0^t d\tau\, \hat{H}_{SB}(\tau)\right)\right]\hat{\rho}_B^{\mathrm{eq}}\right],$$

Redfield

Calculation time: ◐ ○ ○ ○ ○ Accuracy: ● ○ ○ ○ ○

$$\mathrm{I}^{\mathrm{A}}_{\alpha\beta}(t) = \delta_{\alpha\beta} e^{-i\varepsilon_\alpha t - g_{\alpha\alpha\alpha\alpha}(t) - R_\alpha(t)},$$

with

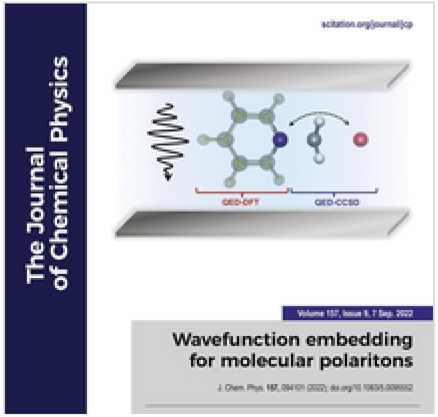
$$R_\alpha^{\mathrm{sR}} = \sum_\beta \mathrm{Re}\int_0^\infty dt\, e^{i\omega_{\alpha\beta}t} C_{\alpha\beta\beta\alpha}(t),$$

Gelzinis *et al*. 2015. J. Chem. Phys. 142(15)

Approximate methods

Volume 157, Issue 9

7 September 2022



RESEARCH ARTICLE | SEPTEMBER 07 2022

Accuracy of approximate methods for the calculation of absorption-type linear spectra with a complex system–bath coupling

J. A. Nöthling; Tomáš Mančal; T. P. J. Krüger

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J. Chem. Phys. 157, 095103 (2022)

https://doi.org/10.1063/5.0100977 **Article history**

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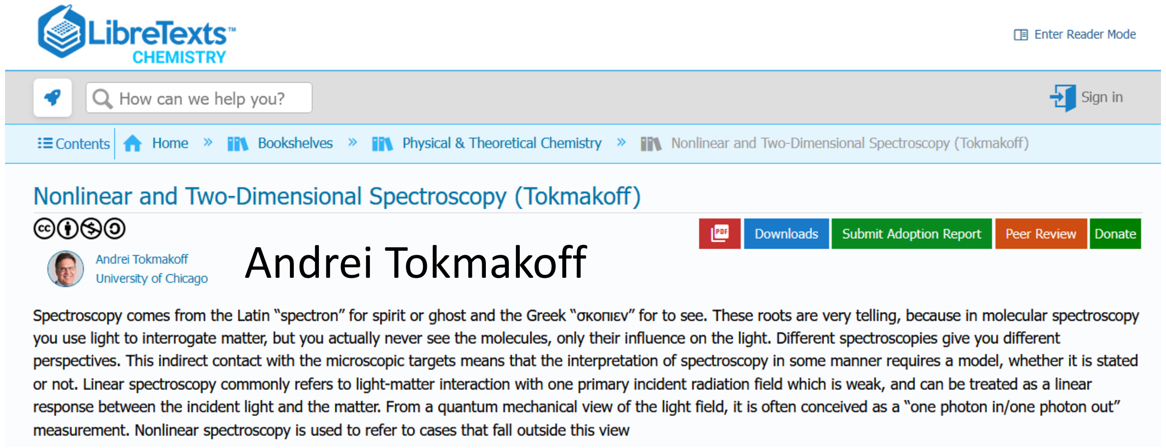

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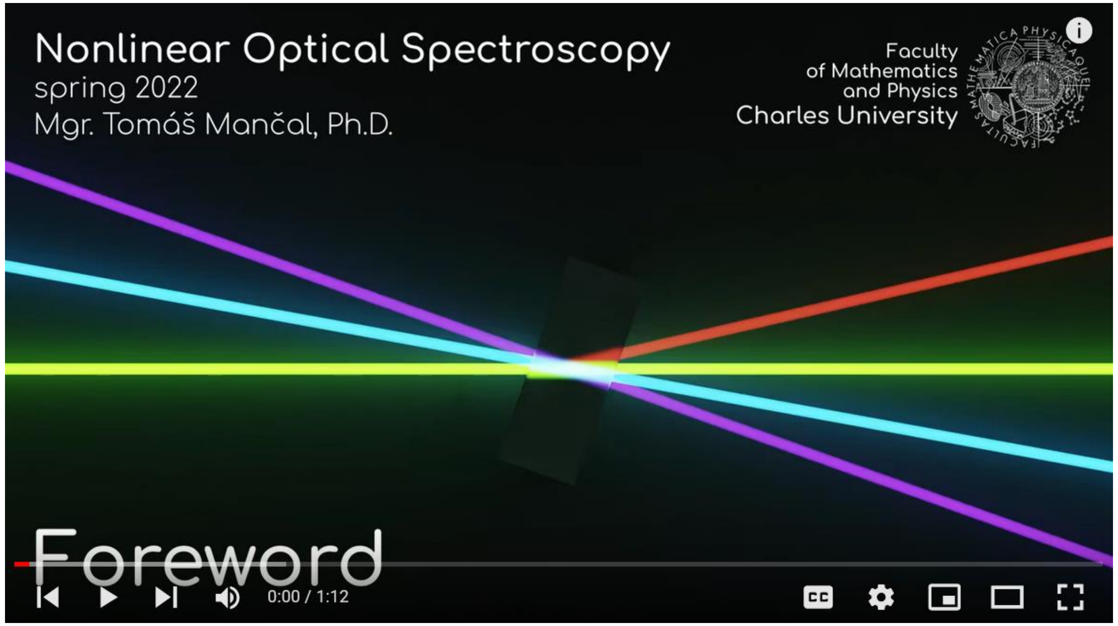
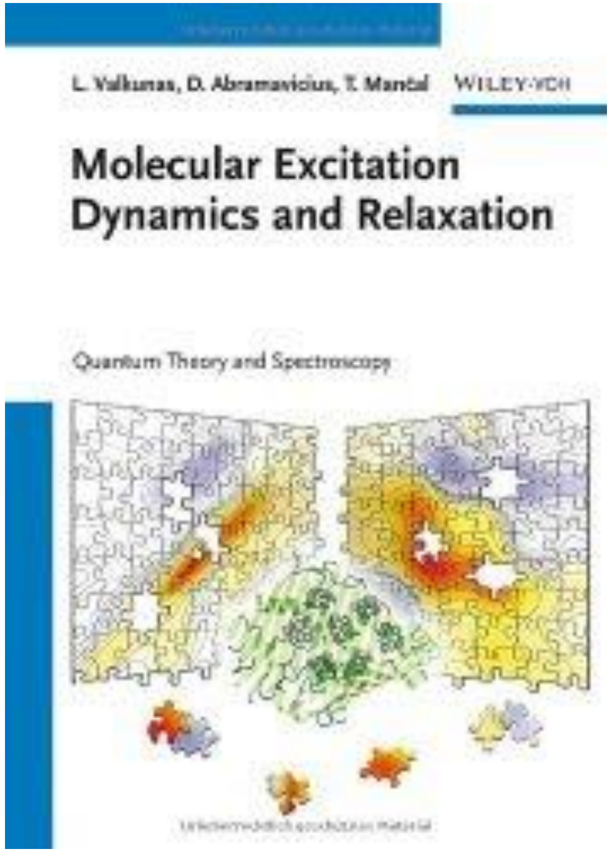
Andrei Tokmakoff
University of Chicago

Spectroscopy comes from the Latin "spectron" for spirit or ghost and the Greek "σκοπιεν" for to see. These roots are very telling, because in molecular spectroscopy you use light to interrogate matter, but you actually never see the molecules, only their influence on the light. Different spectroscopies give you different perspectives. This indirect contact with the microscopic targets means that the interpretation of spectroscopy in some manner requires a model, whether it is stated or not. Linear spectroscopy commonly refers to light-matter interaction with one primary incident radiation field which is weak, and can be treated as a linear response between the incident light and the matter. From a quantum mechanical view of the light field, it is often conceived as a "one photon in/one photon out" measurement. Nonlinear spectroscopy is used to refer to cases that fall outside this view

Andrei Tokmakoff



Tomáš Mančal, Charles University, Prague. On YT



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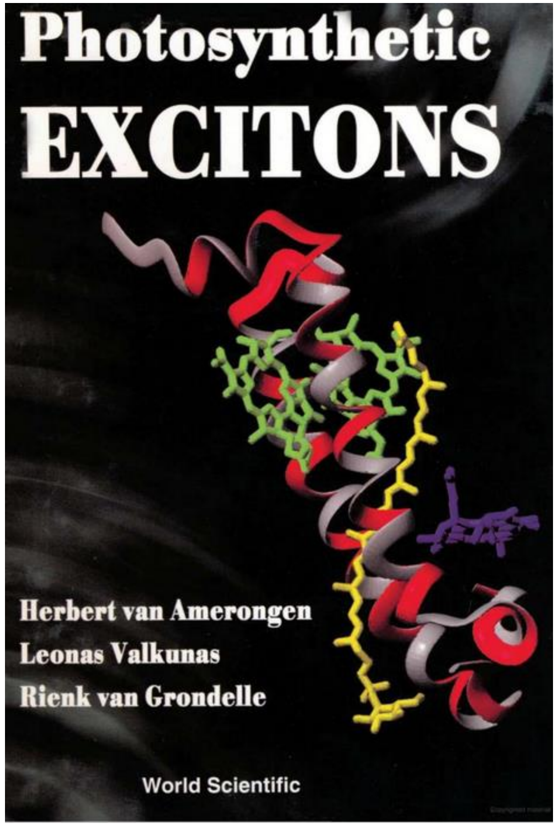
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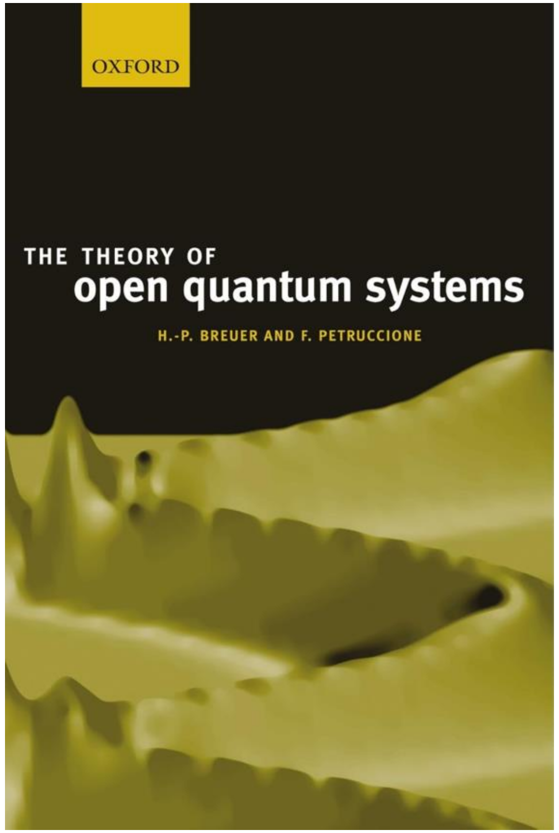
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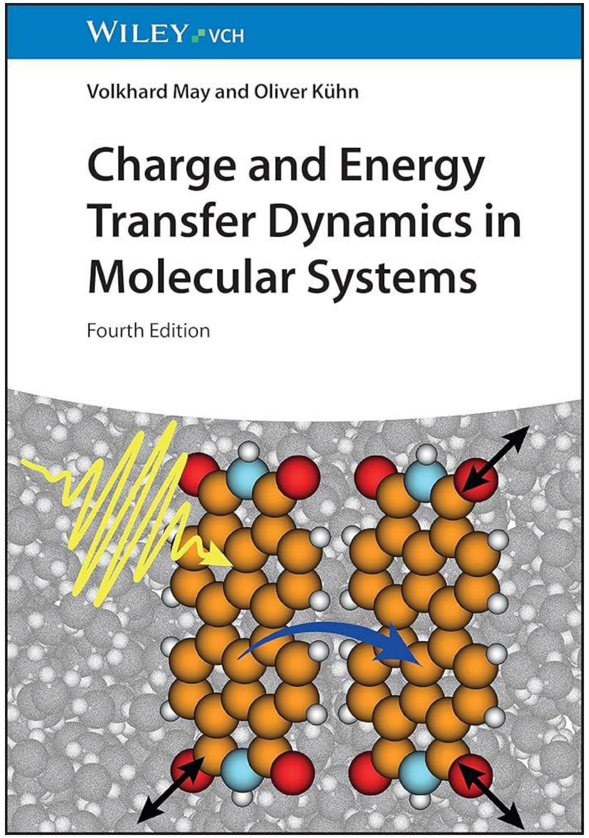
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