Self-Consistent Method for Studying Excitation Energy Transfer in Multichromophoric Systems

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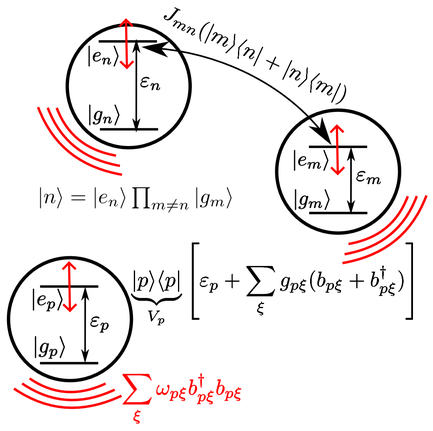
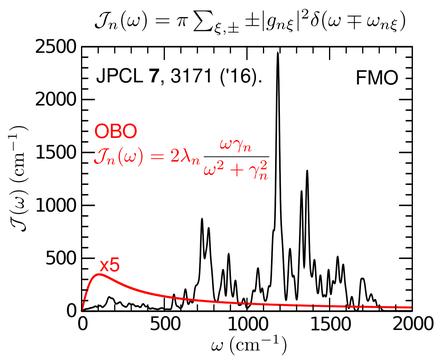
Introduction

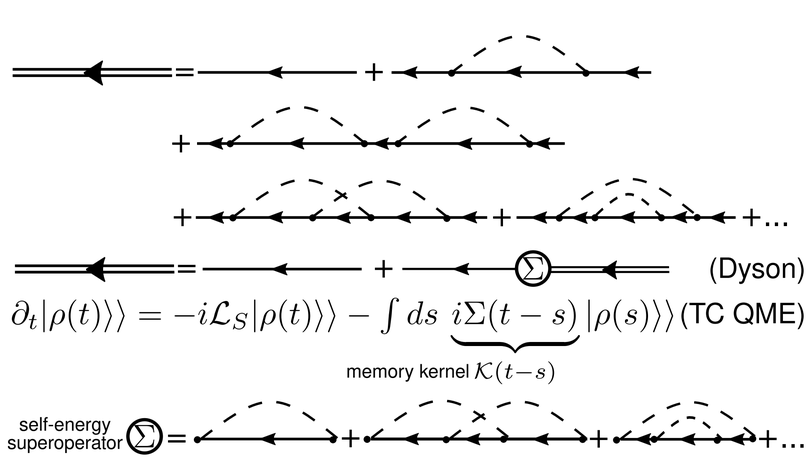
- molecular aggregates as light-harvesting units
  - * photosynthetic pigment–protein complexes
  - * organic photovoltaics
- the excitation energy transfer (EET) is the primary process of the light-to-charge conversion
- the Frenkel–Holstein model $H = H_S + H_B + H_{S-B}$
  - * H_S: resonantly coupled 2-level systems
  - * H_B: harmonic oscillators
  - * H_{S-B}: linear in exciton densities and oscillator coordinates



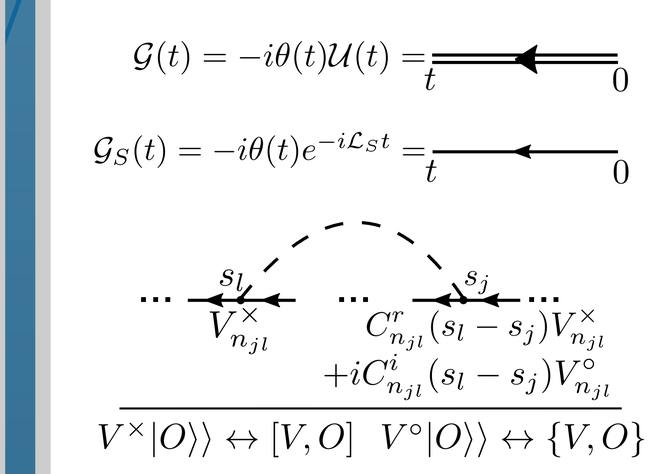


- the spectral density $\mathcal{J}_n(\omega)$ / the bath correlation function $C_n(t)$
  - * fast intramolecular vibrations and slow protein motions
- $W(0) = \rho(0)\rho_B^{\rm eq}$ (Hilbert) $\implies$ $|\rho(t)\rangle\rangle = \mathcal{U}(t)|\rho(0)\rangle\rangle$ (Liouville)
- $\mathcal{U}(t) = e^{-i\mathcal{L}_S t}\,{\rm Tr}_B\left\{\mathcal{T}_t\, e^{-i\int_0^t ds\, \mathcal{L}^{(I)}_{S-B}(s)}\rho_B^{\rm eq}\right\}$
  - * Wick's theorem: $(2k-1)!!$ identical terms $\propto \mathcal{L}^{2k}_{S-B}$
- $\mathcal{U}(t) = e^{-i\mathcal{L}_S t}\,\mathcal{T}_t\, e^{-\Phi(t)}$
  - * $C_n(t) = \Sigma_m c_{n,m}\, e^{-\mu_{n,m}t}$: hierarchical equations of motion (HEOM)
- goal: **develop a computationally efficient and reliable approximation to $\mathcal{U}(t)$ for arbitrary $\mathcal{J}_n(\omega)$ [1]**

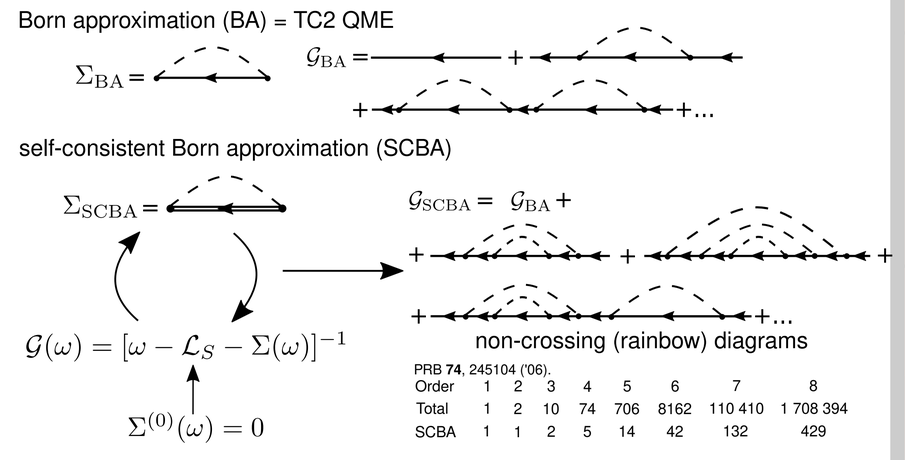
Diagrammatic theory



Building blocks



Resummation in the ω-domain



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Order	1	2	3	4	5	6	7	8
Total	1	2	10	74	706	8162	110 410	1 708 394
SCBA	1	1	2	5	14	42	132	429

Dimer model. Pure dephasing—analytics

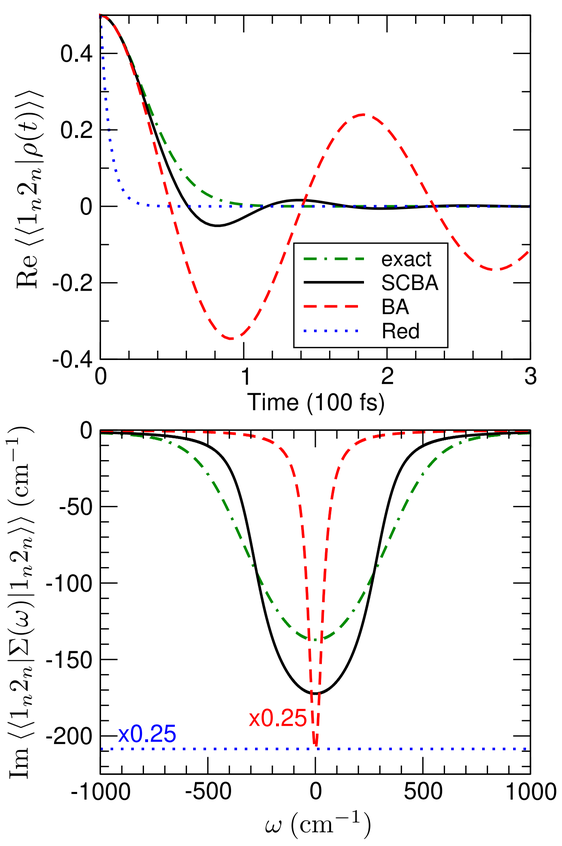
$$H_S = \begin{pmatrix} \Delta\varepsilon & J \\ J & 0 \end{pmatrix}, \rho(0) = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

- overdamped Brownian oscillator SD $\mathcal{J}(\omega) = 2\lambda_{\rm ph}\frac{\omega\gamma_{\rm ph}}{\omega^2 + \gamma^2_{\rm ph}}$

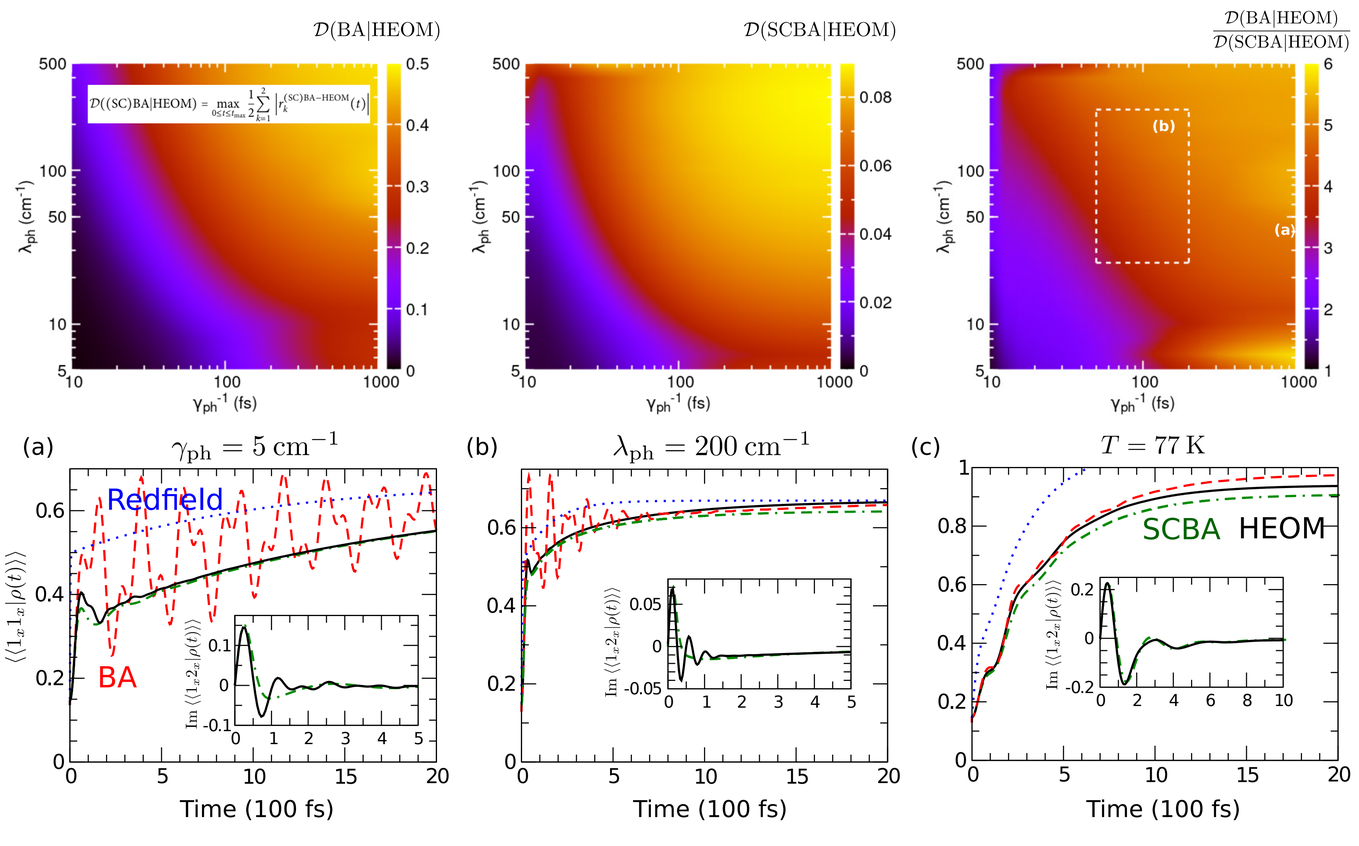
Parameter (unit)	Value
$\Delta\varepsilon$ (cm^{-1})	100
J (cm^{-1})	50
$\lambda_{\rm ph}$ (cm^{-1})	40
$\gamma_{\rm ph}$ (cm^{-1})	40
T (K)	300

- $J = \Delta\varepsilon = 0$
  - * $2\pi T \gg \gamma_{\rm ph}$

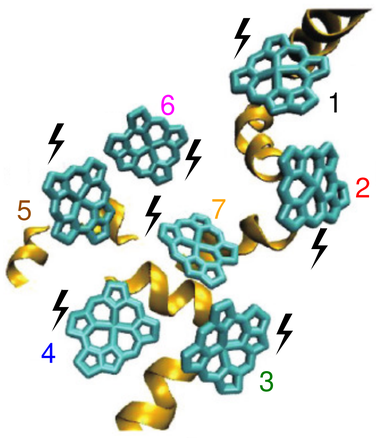
$$\langle\langle 1_n 2_n|\Sigma^{\rm exact}_{\rm SCBA}(\omega)|1_n 2_n\rangle\rangle = \cfrac{4\lambda_{\rm ph}T}{\omega + i\gamma_{\rm ph} - \cfrac{\left\{\begin{matrix}2\\1\end{matrix}\right\}\cdot 4\lambda_{\rm ph}T}{\omega + 2i\gamma_{\rm ph} - \cfrac{\left\{\begin{matrix}3\\1\end{matrix}\right\}\cdot 4\lambda_{\rm ph}T}{\omega + 3i\gamma_{\rm ph} - \cdots}}}$$



(SC)BA for slow environment, strong interaction, low temperature



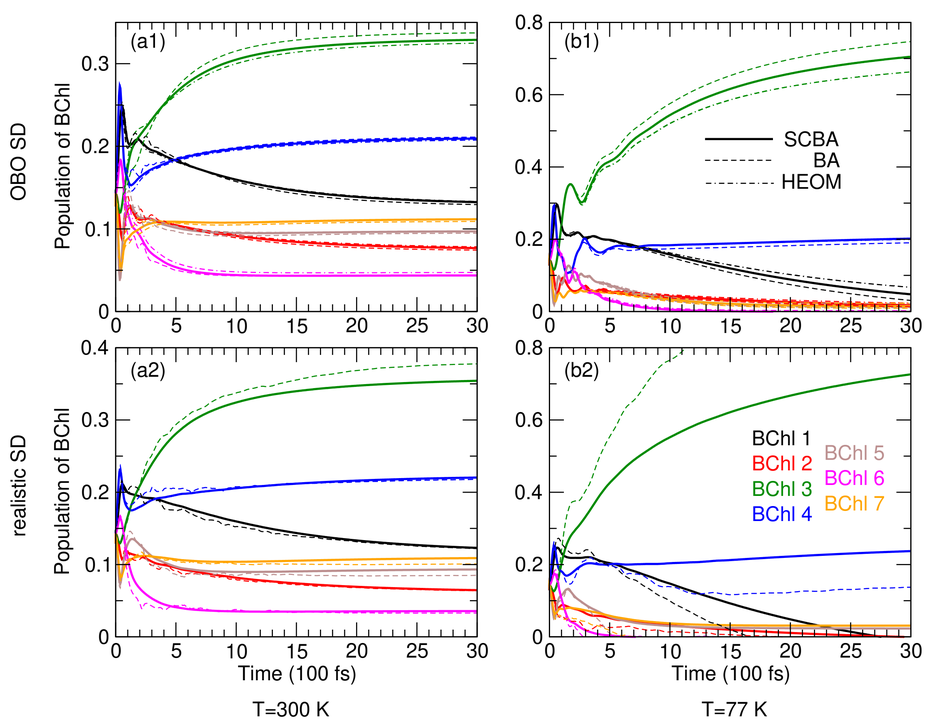
7-site FMO model



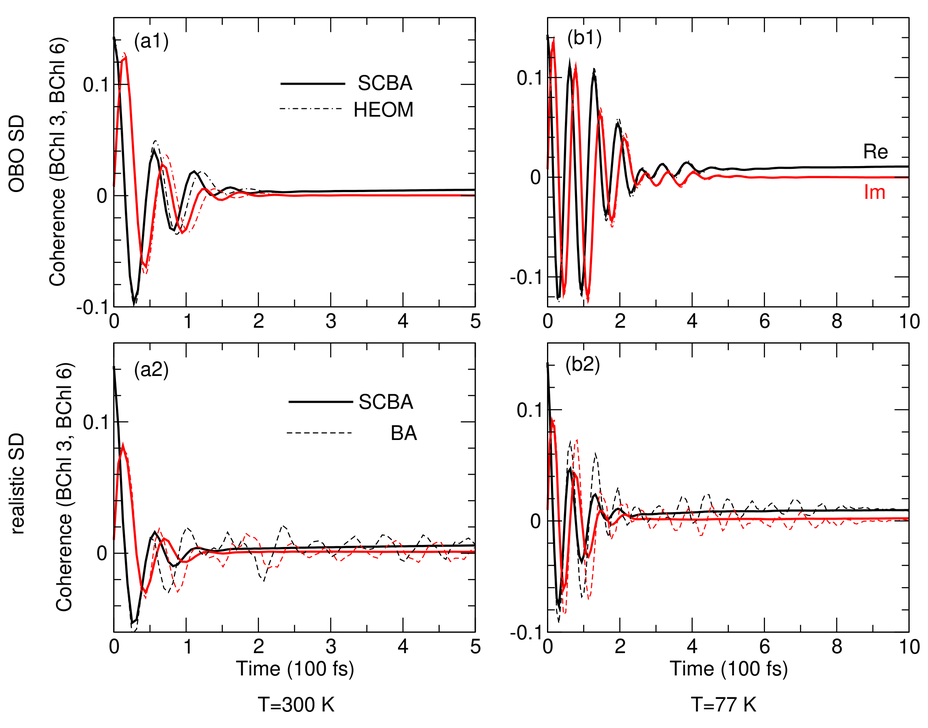
$$\rho(0) = \frac{1}{7}\sum_{n=1}^{7}|n\rangle\langle n|$$

OBO SD	realistic SD
$\lambda_{\rm ph} = 35$ cm^{-1}	see Intro
$\gamma^{-1}_{\rm ph} = 50$ fs	

EET in FMO complex: BChl populations



EET in FMO complex: Coherences



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References

[1] V. Janković and T. Mančal, J. Chem. Phys. **161**, 204108 ('24).