Non-Equilibrium Thermo Field Dynamics and Tensor-Train Approaches to Closed and Open System Evolution: Theory, Implementation and Application

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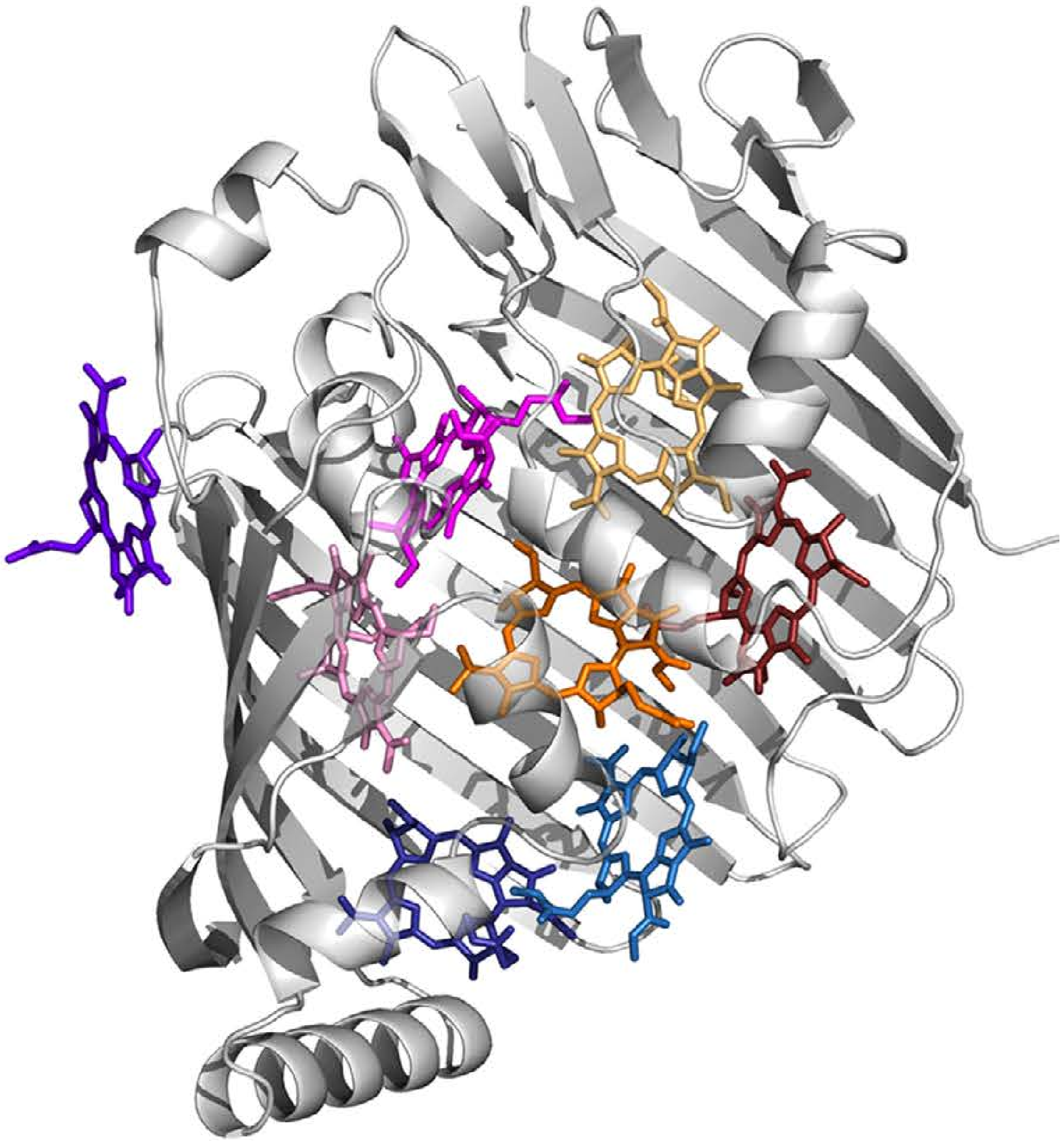
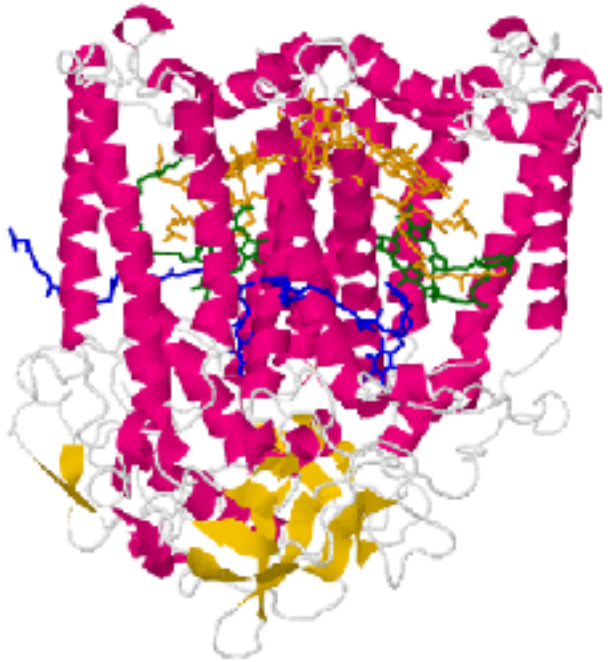
The chemical systems

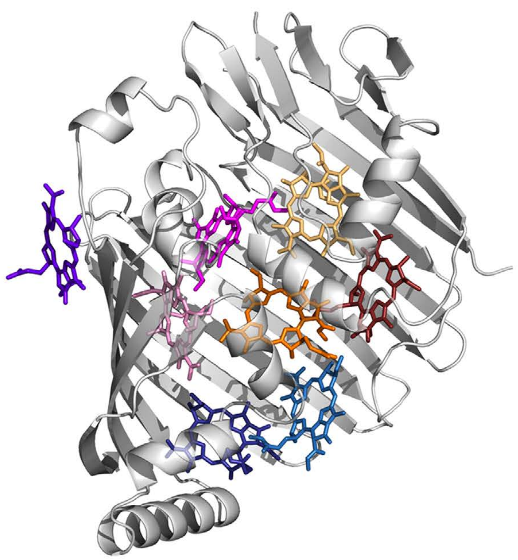


Exciton Energy Transfer

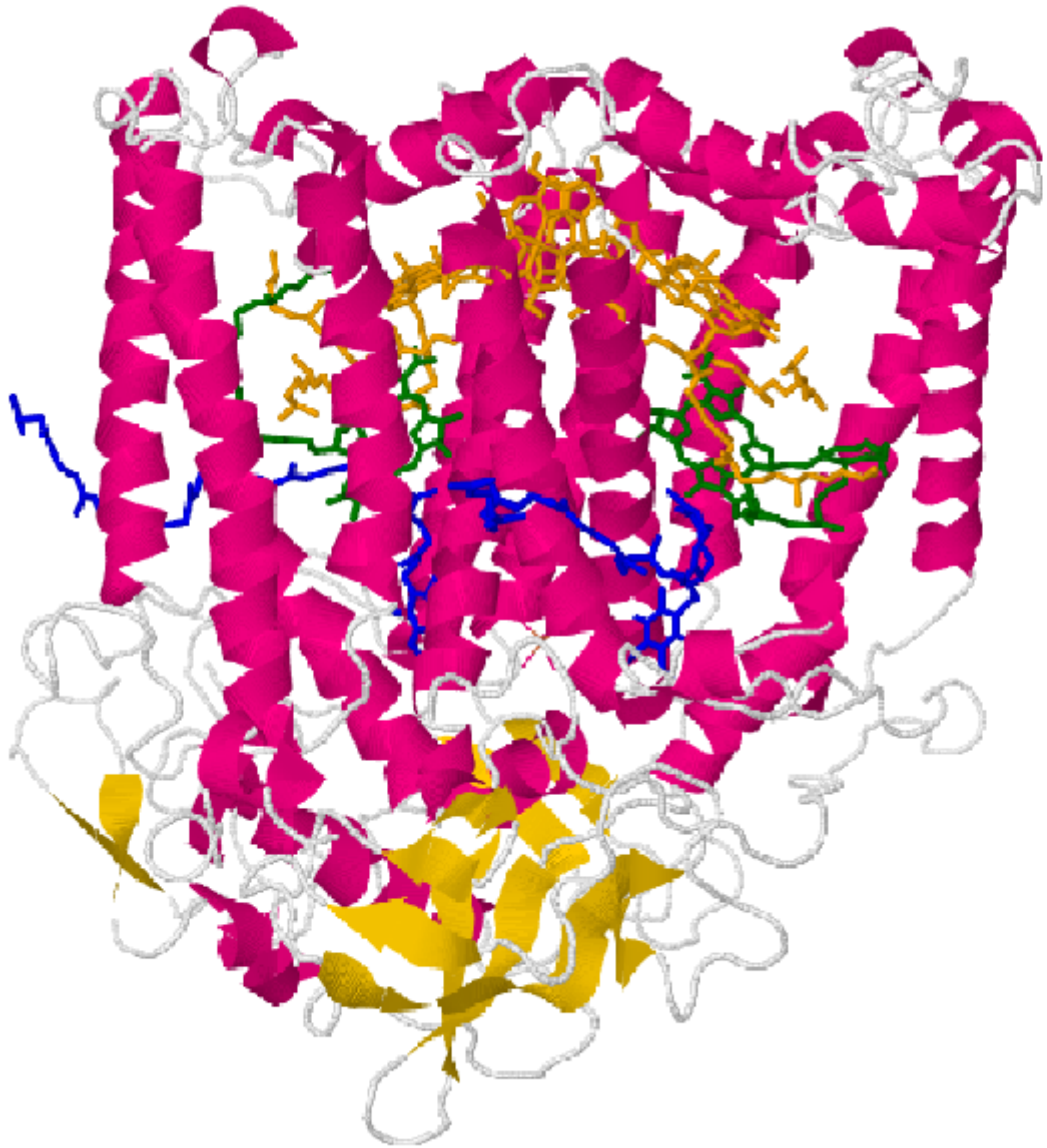


Charge Transfer

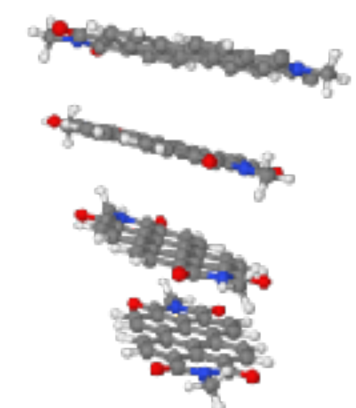
The chemical systems



Exciton Energy Transfer

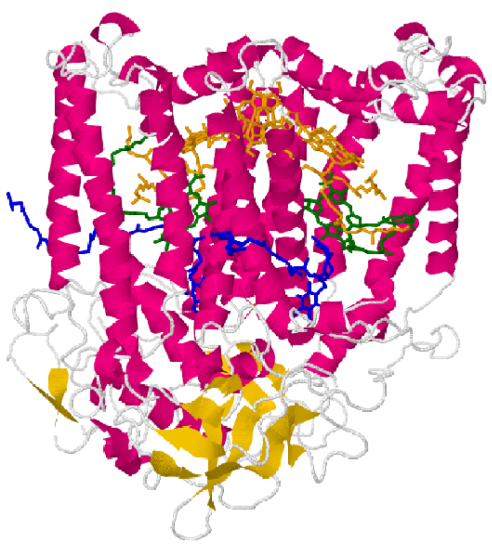


Charge Transfer

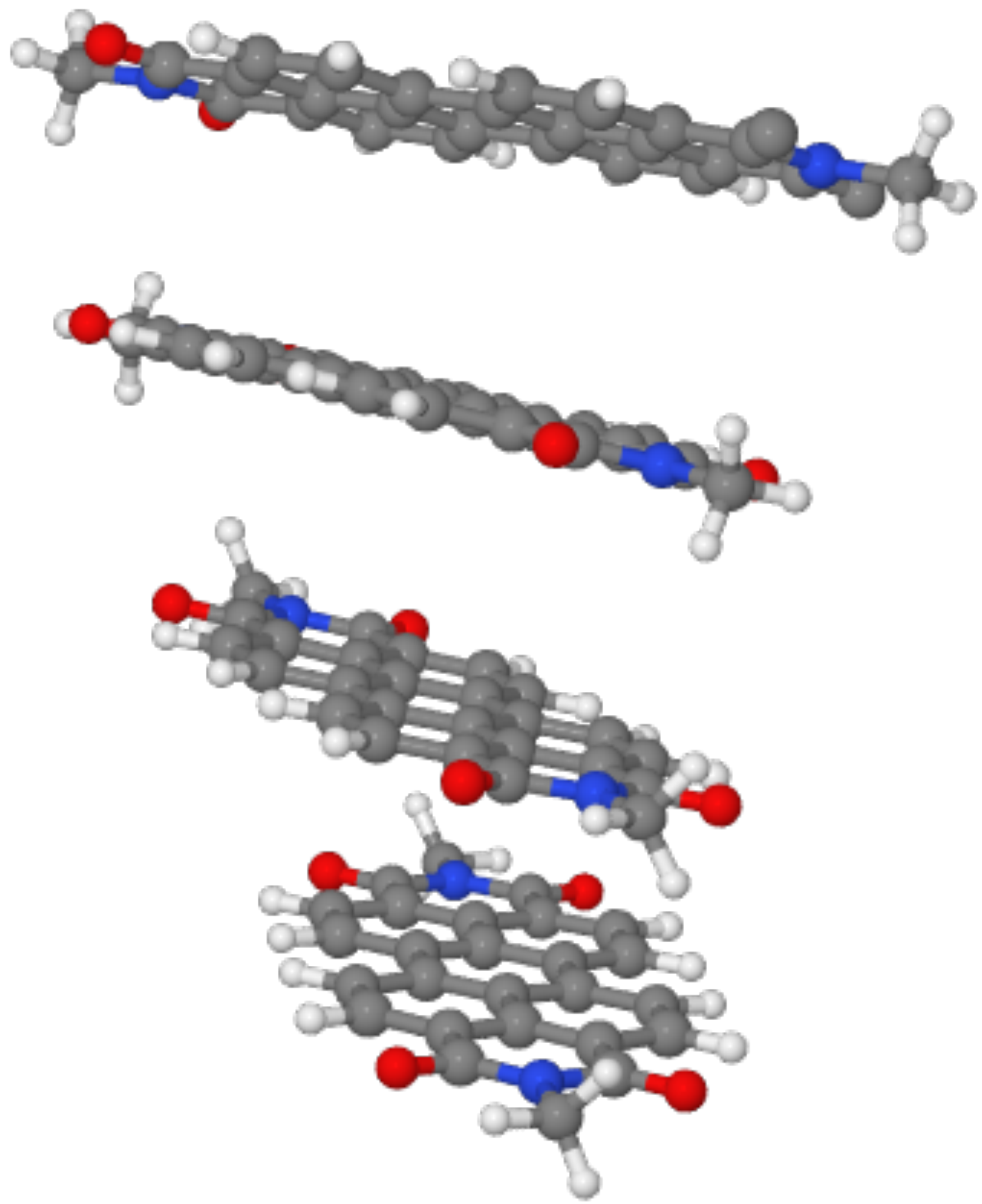


EET/CT

The chemical systems



Charge Transfer



EET/CT

A simple "universal" model

$$H = \sum_{n}^{N} \varepsilon_n |n\rangle\langle n| + \sum_{<n,m>} V_{nm} |n\rangle\langle m| + \text{H.c.}$$

excitons/CT states

$$+ \sum_{i}^{d} \omega_i a_i^\dagger a_i$$

vibrations

$$+ \sum_{n}^{N} \sum_{i}^{d} \frac{g_i^{(n)}}{\sqrt{2}} (a_i^\dagger + a_i) |n\rangle\langle n|$$

ex/CT-vibration

A simple "universal" model

$$H = \sum_{n}^{N} \varepsilon_n |n\rangle\langle n| + \sum_{<n,m>} V_{nm} |n\rangle\langle m| + \text{H.c.}$$

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$$+ \sum_{i}^{d} \omega_i a_i^\dagger a_i$$

vibrations

$$+ \sum_{n}^{N} \sum_{i}^{d} \frac{g_i^{(n)}}{\sqrt{2}} (a_i^\dagger + a_i) |n\rangle\langle n|$$

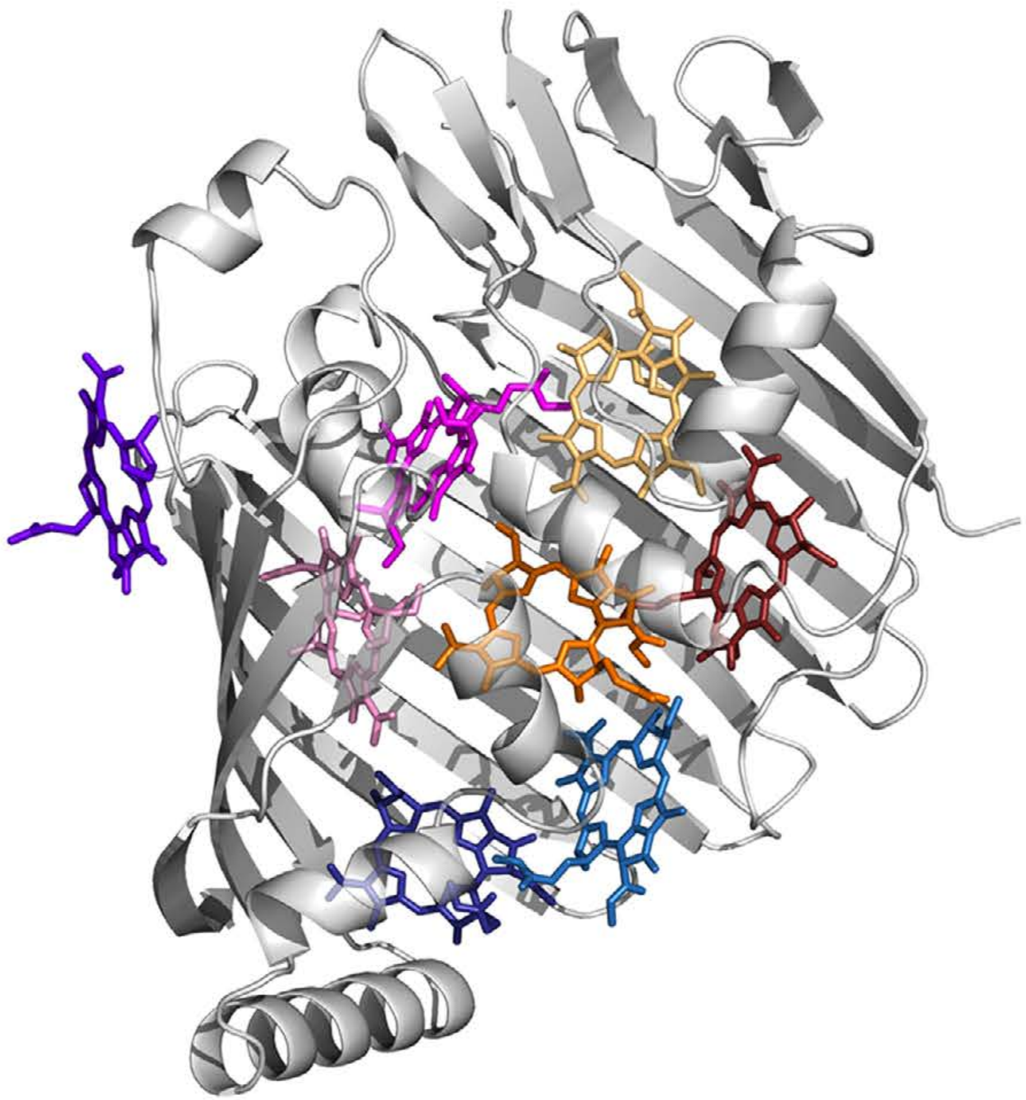
ex/CT-vibration

g_i^n: molecule specific; obtained from quantum chemistry calculations; experimental data.

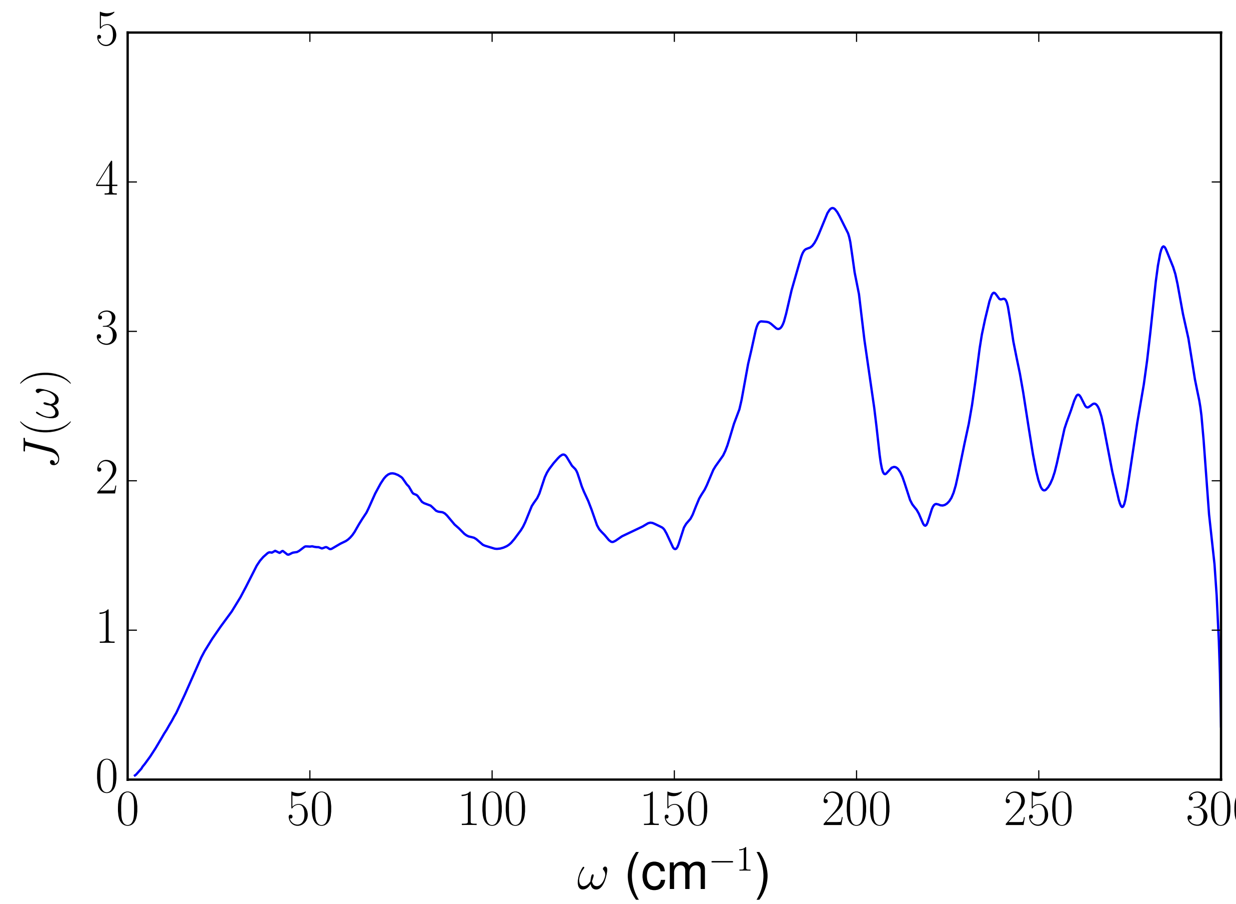
Dynamical information encoded into the spectral density

$$J(\omega) \propto \sum_i g_i^2 \delta(\omega - \omega_i)$$

Vibronic Dynamics

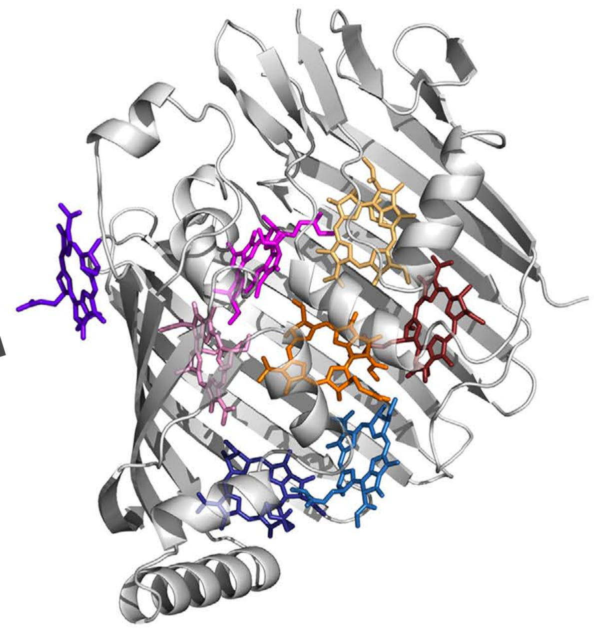


Experimental spectral density from FLN
(Wendling 2000)



Highly structured spectral density

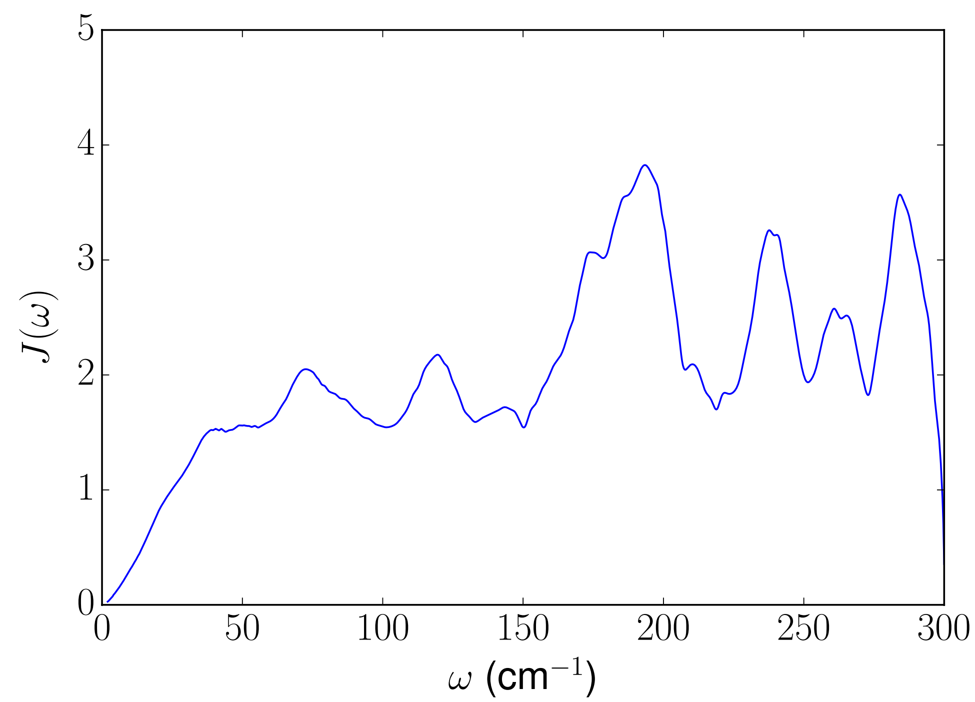
Vibronic Dynamics with arbitrary spectral densities



Full

System

(*closed*)

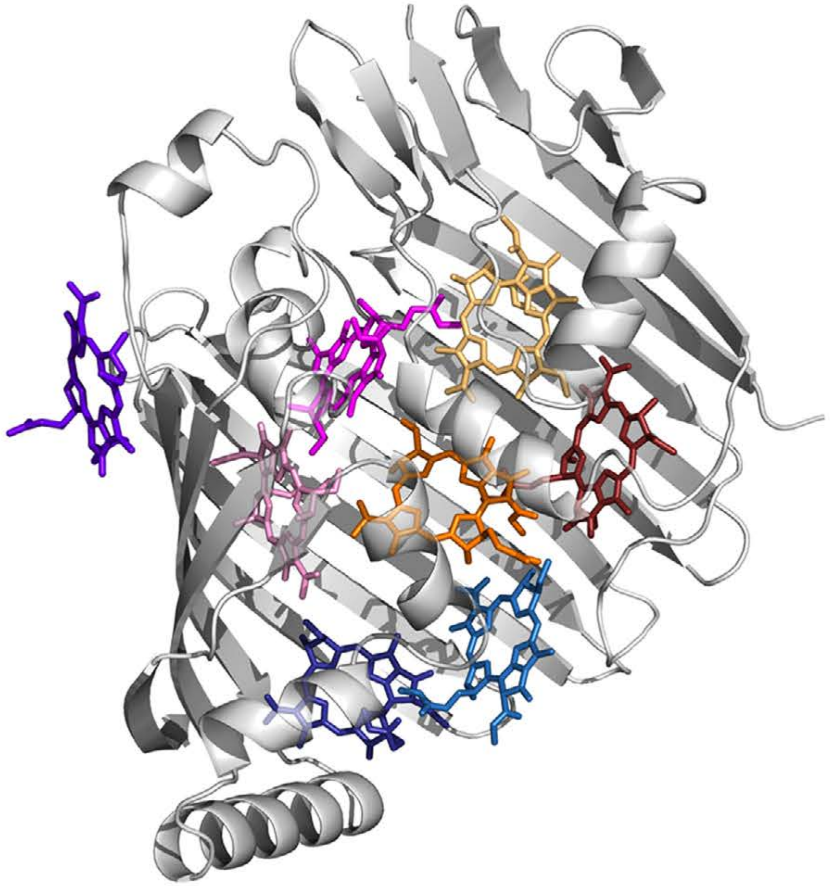


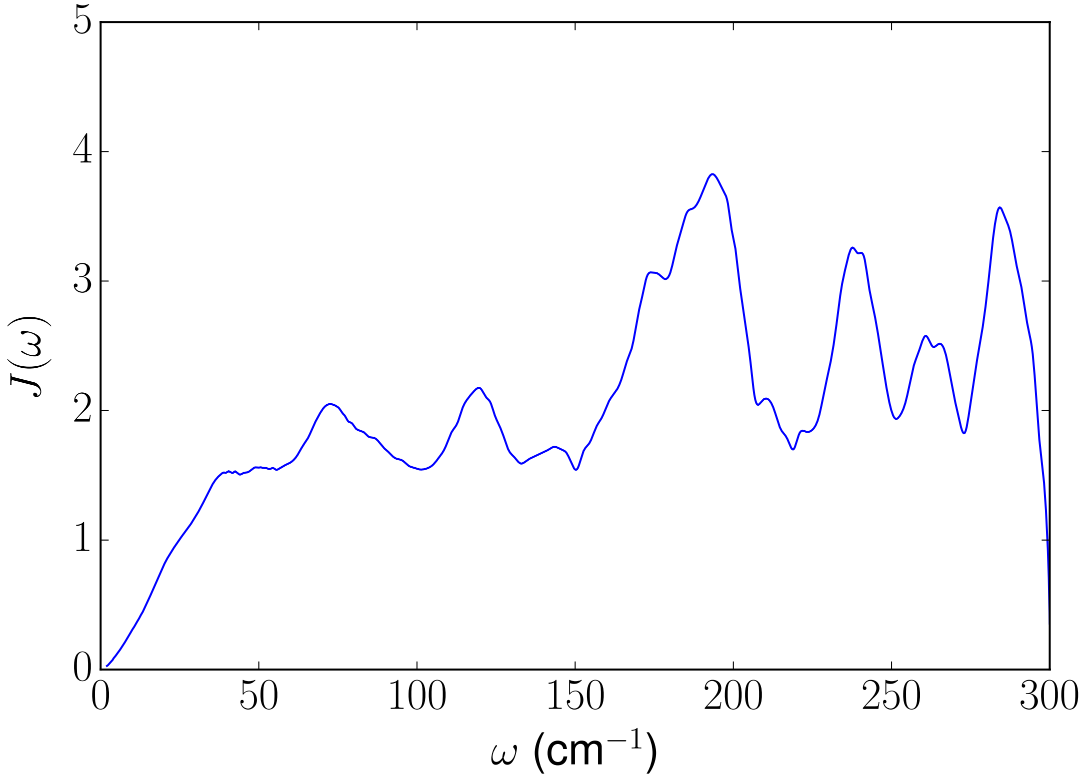
Reduced

System

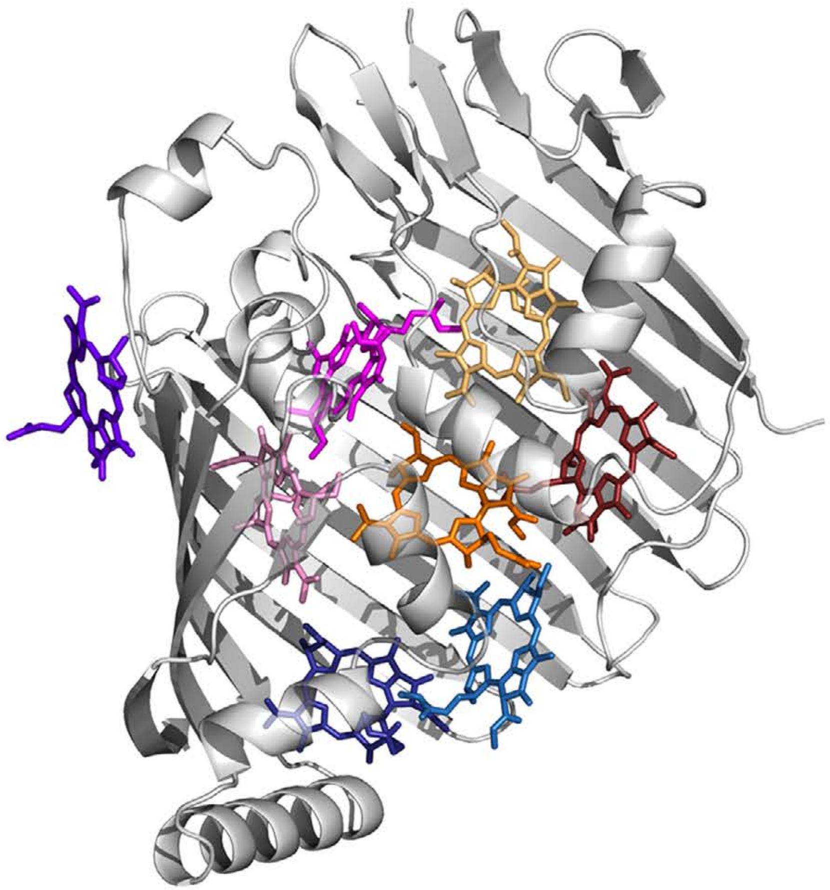
(*open*)

Quantum dynamics of closed systems

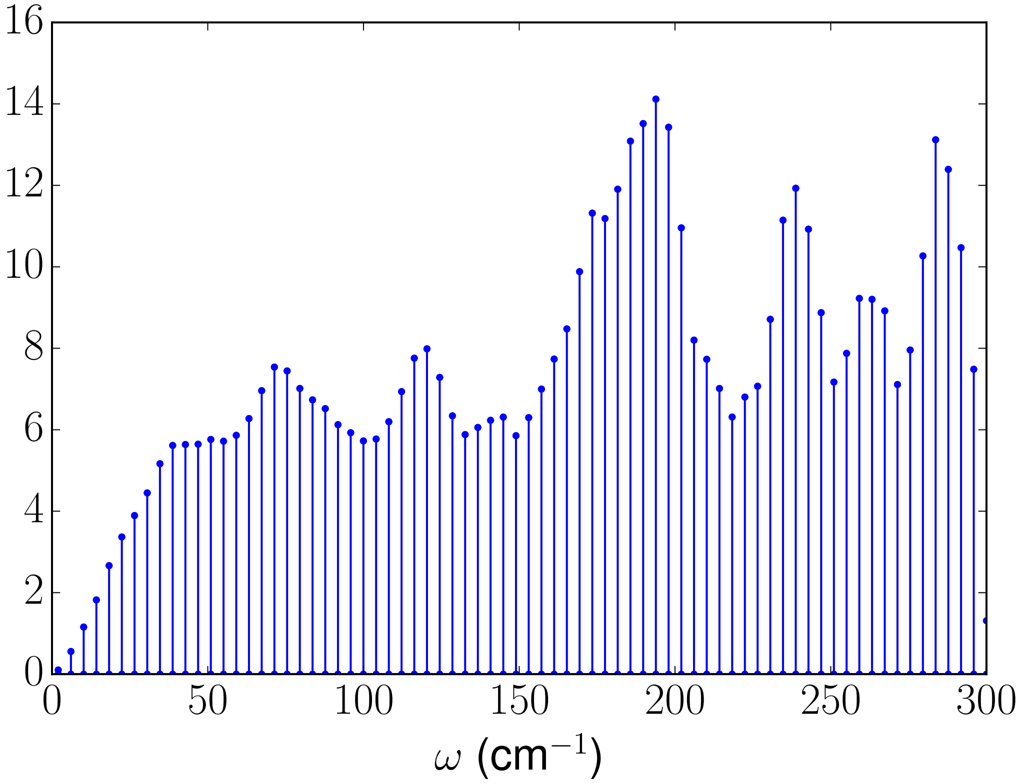




Quantum dynamics of closed systems

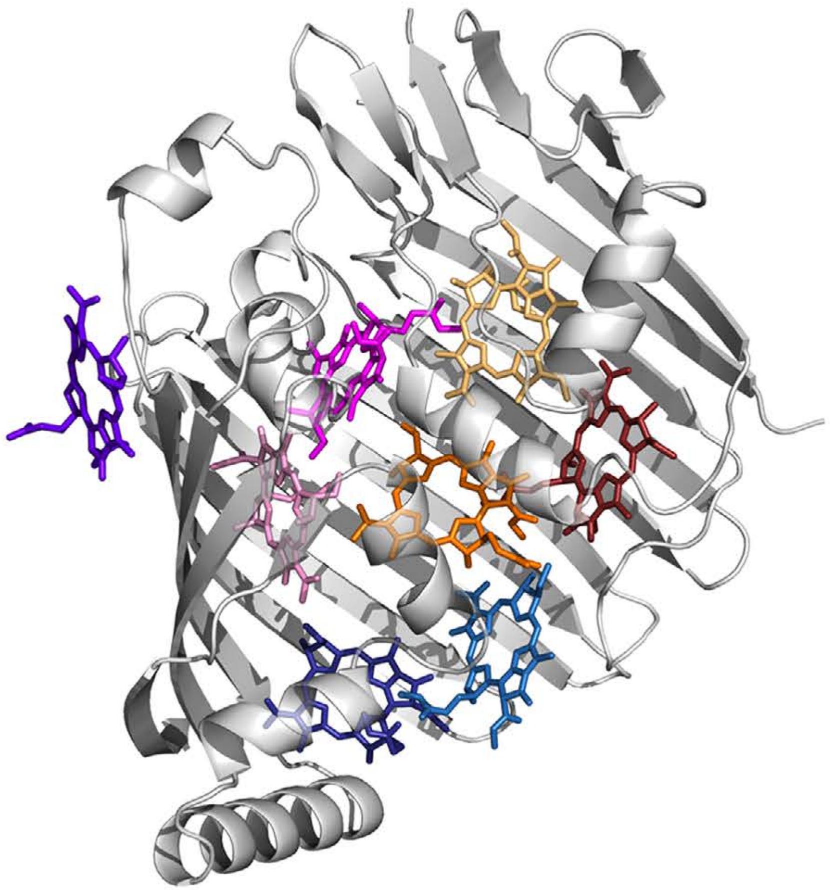


$$\omega_i a_i^\dagger a_i + \frac{g_i^{(n)}}{\sqrt{2}}(a_i^\dagger + a_i)|n\rangle\langle n|$$

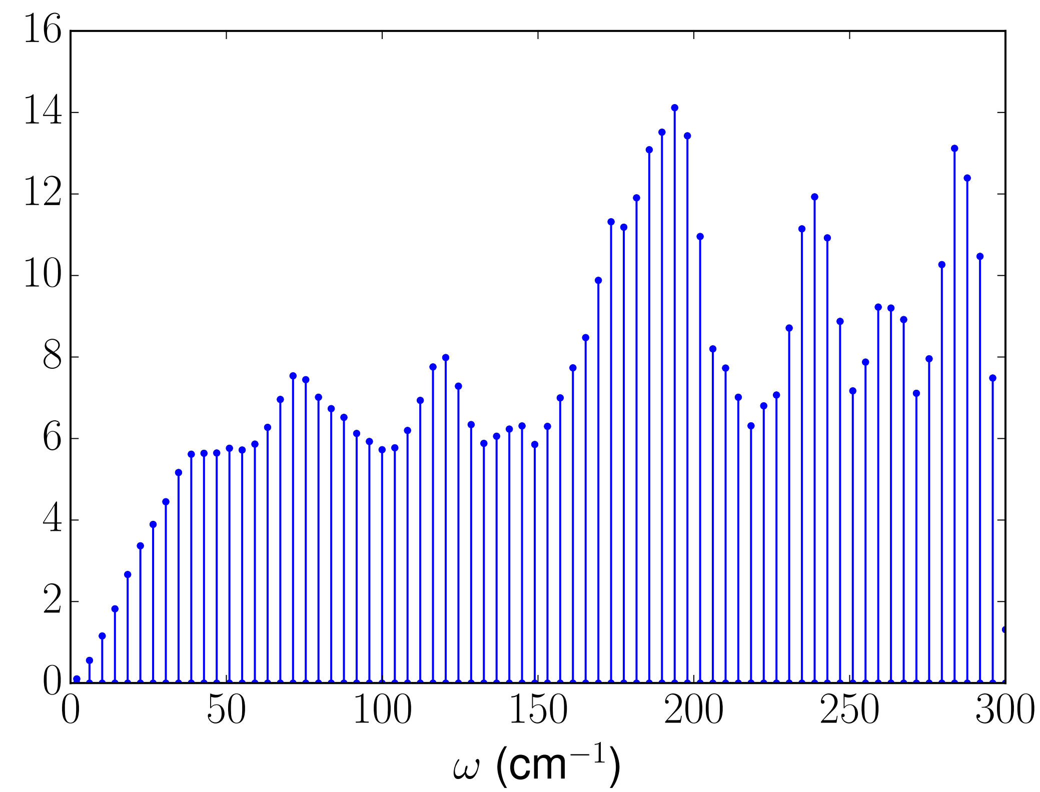


Highly structured spectral densities can be discretised

Quantum dynamics of closed systems



$$\omega_i a_i^\dagger a_i + \frac{g_i^{(n)}}{\sqrt{2}}(a_i^\dagger + a_i)|n\rangle\langle n|$$



Highly structured spectral densities can be discretised

The number of degrees of freedom becomes very large

Quantum dynamics of closed systems

$$\langle A(t)\rangle = \left\langle \psi(t) \middle| A \middle| \psi(t) \right\rangle$$

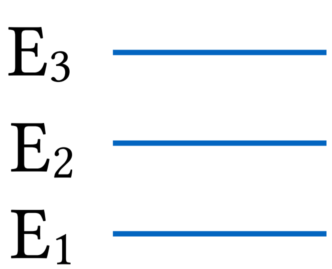
Quantum dynamics of closed systems

$$\langle A(t)\rangle = \langle \psi(t)|A|\psi(t)\rangle$$

Many low frequency vibrations…

we need temperature effects

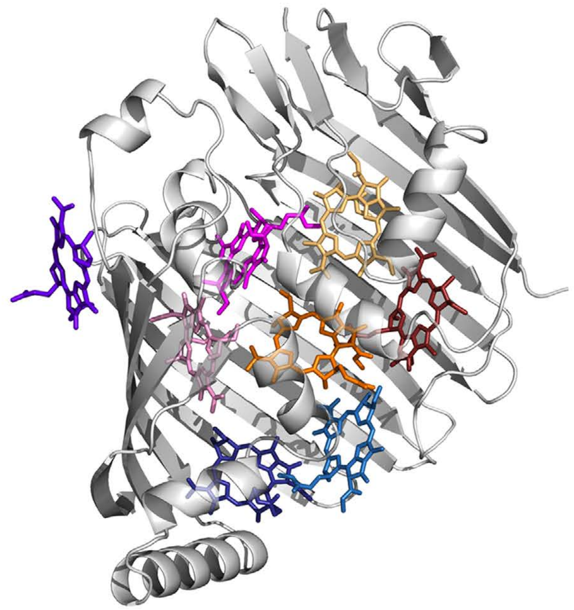
$$p_i \propto e^{-\beta E_i}$$



$$\langle A(t)\rangle = \sum_i p_i \langle \psi_i(t)|A|\psi_i(t)\rangle$$

$$i\hbar\frac{\partial}{\partial t}|\psi_i(t)\rangle = H|\psi_i(t)\rangle$$

Density Matrix: Liouville-von Neumann Equation



$\mathcal{H}$

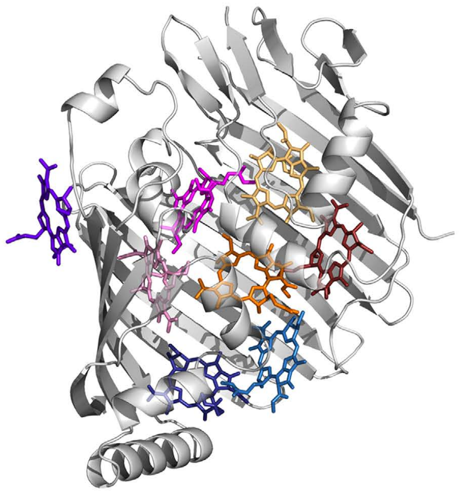
Physical space

$p, q, a, a^\dagger$

$$i\frac{\partial}{\partial t}\rho = [H,\rho] = H\rho - \rho H$$

$$\rho(0) \propto e^{-\beta H_0}$$

Non-Equilibrium Thermo-Field Dynamics



$\mathcal{H}$

Physical space

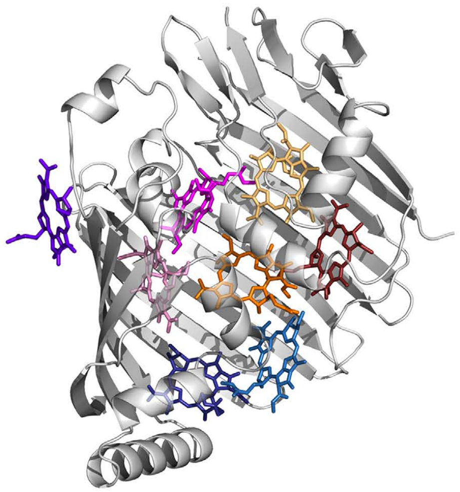
$p, q, a, a^\dagger$

$\otimes$

$\tilde{\mathcal{H}}$

Tilde space

$\tilde{p}, \tilde{q}, \tilde{a}, \tilde{a}^\dagger$



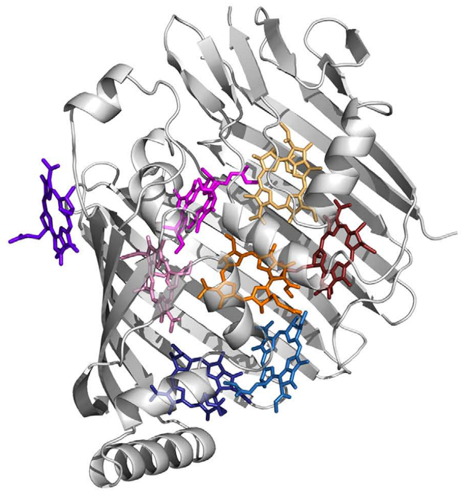
$$i\frac{\partial}{\partial t}|\rho\rangle = (H - \tilde{H})|\rho\rangle$$

$$\rho \sum_n |n\tilde{n}\rangle = \rho|I\rangle \rightarrow |\rho\rangle$$

matrix — *vector* $\in \mathcal{H} \otimes \tilde{\mathcal{H}}$ — *vector* $\in \mathcal{H} \otimes \tilde{\mathcal{H}}$

See also Zwolak and Vidal PRL 2004

Non-Equilibrium Thermo-Field Dynamics



$\mathcal{H}$

Physical space

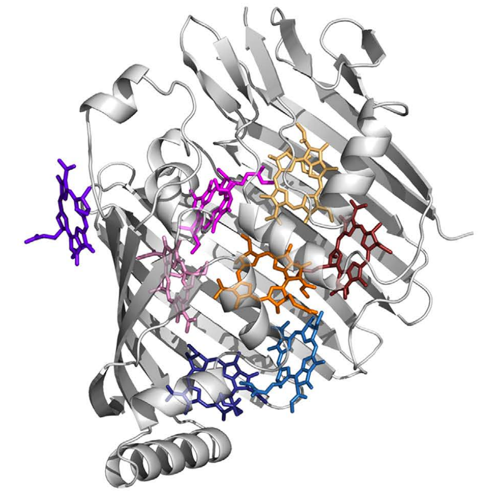
$p, q, a, a^\dagger$

$\otimes$

$\tilde{\mathcal{H}}$

Tilde space

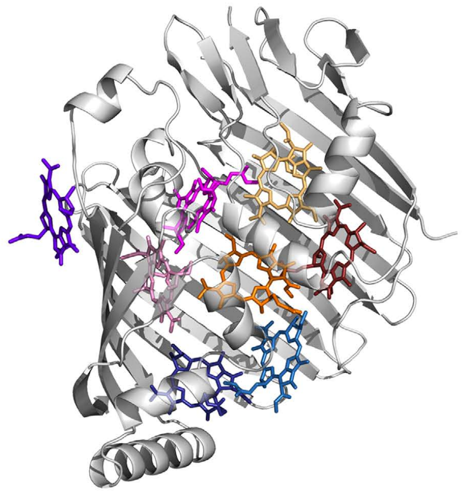
$\tilde{p}, \tilde{q}, \tilde{a}, \tilde{a}^\dagger$



$$i\frac{\partial}{\partial t}|\rho\rangle = (H - \tilde{H})|\rho\rangle$$

$$\mathrm{Tr}\{\rho(t)A\} = \langle I|A|\rho\rangle$$

Schrödinger equation at finite temperature



$\mathcal{H}$

Physical space

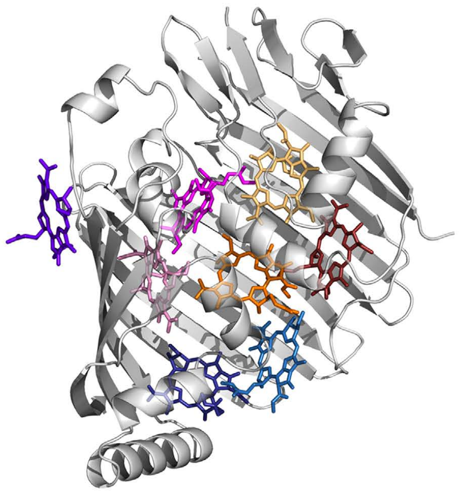
$p, q, a, a^\dagger$

$\otimes$

$\tilde{\mathcal{H}}$

Tilde space

$\tilde{p}, \tilde{q}, \tilde{a}, \tilde{a}^\dagger$



$$i\frac{\partial}{\partial t}\big|\varphi(t)\big\rangle = H_\theta\big|\varphi(t)\big\rangle \qquad \big|\varphi(0)\big\rangle = \big|\mathbf{e}\big\rangle\big|\mathbf{0}\big\rangle$$

$$\mathrm{Tr}\{\rho(t)A\} = \big\langle\varphi(t)\big|A_\theta\big|\varphi(t)\big\rangle$$

Schrödinger equation at finite temperature

$$i\frac{\partial}{\partial t}\big|\varphi(t)\big\rangle = H_\theta\big|\varphi(t)\big\rangle \qquad \big|\varphi(0)\big\rangle = \big|\boldsymbol{e}\big\rangle\big|\boldsymbol{0}\big\rangle$$

$$\mathrm{Tr}\{\rho(t)A\} = \big\langle\varphi(t)\big|A_\theta\big|\varphi(t)\big\rangle$$

$$\boxed{H_\theta = e^{iG}He^{-iG}}$$

$$e^{-iG}$$

Bogoliubov thermal transformation: depends on temperature

$$G = -i\sum_k \theta_k(a_k\tilde{a}_k - a_k^\dagger\tilde{a}_k^\dagger) \qquad \theta_k = \mathrm{arctanh}(e^{-\beta\omega_k/2})$$

The TFD recipe

- Write the Hamiltonian operator
- Apply the thermal transformation

$$H_\theta = e^{iG} H e^{-iG}$$

- Solve the TFD-TDSE

$$i\frac{\partial}{\partial t}\big|\varphi(t)\big\rangle = H_\theta\big|\varphi(t)\big\rangle \qquad \big|\varphi(0)\big\rangle = \big|\boldsymbol{e}\big\rangle\big|\mathbf{0}\big\rangle$$

- Compute the desired expectation value

$$\langle A(t)\rangle = \big\langle\varphi(t)\big|A_\theta\big|\varphi(t)\big\rangle \quad \text{with} \quad A_\theta = e^{iG} A e^{-iG}$$

What do we gain?

Linear coupling model at finite temperature

$$
\begin{aligned}
\boldsymbol{H} &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm}|n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \quad (a_k + a_k^\dagger)
\end{aligned}
$$

Linear coupling model at finite temperature

$$
\begin{aligned}
H \quad &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm} |n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \quad (a_k + a_k^\dagger)
\end{aligned}
$$

$$e^{iG} H e^{-iG} \longrightarrow H_\theta$$

Linear coupling model at finite temperature

$$
\begin{aligned}
\boldsymbol{H_\theta} &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm}|n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \quad (a_k + a_k^\dagger)
\end{aligned}
$$

Linear coupling model at finite temperature

$$
\begin{aligned}
H_\theta &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm} |n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k - \sum_k \omega_k \tilde{a}_k^\dagger \tilde{a}_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \left\{ \left(a_k + a_k^\dagger\right)\cosh(\theta_k) + \left(\tilde{a}_k + \tilde{a}_k^\dagger\right)\sinh(\theta_k) \right\}
\end{aligned}
$$

$$
\begin{aligned}
e^{iG} a_k e^{-iG} &= a_k \cosh(\theta_k) + \tilde{a}_k^\dagger \sinh(\theta_k) \\
e^{iG} \tilde{a}_k e^{-iG} &= a_k^\dagger \sinh(\theta_k) + \tilde{a}_k \cosh(\theta_k)
\end{aligned}
$$

$$
\theta_k = \operatorname{arctanh}(e^{-\beta\omega_k/2})
$$

Linear coupling model at finite temperature

$$
\begin{aligned}
H_\theta =& \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm} |n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k - \sum_k \omega_k \tilde{a}_k^\dagger \tilde{a}_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \left\{ \left(a_k + a_k^\dagger\right) \cosh(\theta_k) + \left(\tilde{a}_k + \tilde{a}_k^\dagger\right) \sinh(\theta_k) \right\}
\end{aligned}
$$

The Hamiltonian becomes temperature dependent. (θ_k)

Schrödinger equation is recovered at zero temperature.

Linear coupling model at finite temperature

$$
\begin{aligned}
H_\theta &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm}|n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k - \sum_k \omega_k \tilde{a}_k^\dagger \tilde{a}_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \left\{ \left(a_k + a_k^\dagger\right)\cosh(\theta_k) + \left(\tilde{a}_k + \tilde{a}_k^\dagger\right)\sinh(\theta_k) \right\}
\end{aligned}
$$

$T \to 0$

$\cosh(\theta_k) \to 1$

$\sinh(\theta_k) \to 0$

The Hamiltonian becomes temperature dependent. (θ_k)

Schrödinger equation is recovered at zero temperature.

Linear coupling model at finite temperature

$$
\begin{aligned}
H_\theta &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n\neq m} V_{nm}|n\rangle\langle m| \\
&+ \sum_k \omega_k a_k^\dagger a_k - \sum_k \omega_k \tilde{a}_k^\dagger \tilde{a}_k \\
&- \sum_{kn} |n\rangle\langle n| \frac{g_{kn}}{\sqrt{2}} \left\{ (a_k + a_k^\dagger)\cosh(\theta_k) + (\tilde{a}_k + \tilde{a}_k^\dagger)\sinh(\theta_k) \right\}
\end{aligned}
$$

$T \to 0$

$\cosh(\theta_k) \to 1$

$\sinh(\theta_k) \to 0$

The Hamiltonian becomes temperature dependent. (θ_k)

Schrödinger equation is recovered at zero temperature.

Final number of degrees of freedom: $N_{\text{el}} + 2N_{\text{vib}}$

Only the number of vibrational degrees of freedom is doubled

How do we solve the dynamical problem?

$$\left|\Psi(t)\right\rangle = \sum_{i_1 i_2 \dots i_N} C(i_1, i_2, \dots, i_N; t)\left|i_1\right\rangle \otimes \left|i_2\right\rangle \cdots \left|i_N\right\rangle$$

Curse of dimensionality

N DoFs, p basis functions per DoF: $M = p^N$

Tensor-Trains (MPS)

Tensor Trains / Matrix Product States

$$\left|\Psi(t)\right\rangle = \sum_{i_1 i_2 \ldots i_N} C(i_1, i_2, \ldots, i_N; t)\left|i_1\right\rangle \otimes \left|i_2\right\rangle \cdots \left|i_N\right\rangle$$

$$C(i_1, \ldots, i_N) \approx C_1(i_1) C_2(i_2) \cdots C_N(i_N)$$

The **cores** $C_k(i_k)$ are $(r_{k-1} \times r_k)$ complex matrices

r_k are called **compression ranks**

Tensor Trains / Matrix Product States

$$\left|\Psi(t)\right\rangle = \sum_{i_1 i_2 \ldots i_N} C(i_1, i_2, \ldots, i_N; t)\left|i_1\right\rangle \otimes \left|i_2\right\rangle \cdots \left|i_N\right\rangle$$

$$C(i_1, \ldots, i_N) \approx C_1(i_1) C_2(i_2) \cdots C_N(i_N)$$

The **cores** $C_k(i_k)$ are $(r_{k-1} \times r_k)$ complex matrices

r_k are called **compression ranks**

$$C(i_1, \ldots, i_N) = \sum_{\alpha_0 \alpha_1 \cdots \alpha_N} C_1(\alpha_0, i_1, \alpha_1) C_2(\alpha_1, i_2, \alpha_2) \cdots C_N(\alpha_{N-1}, i_N, \alpha_N)$$

Tensor Trains / Matrix Product States

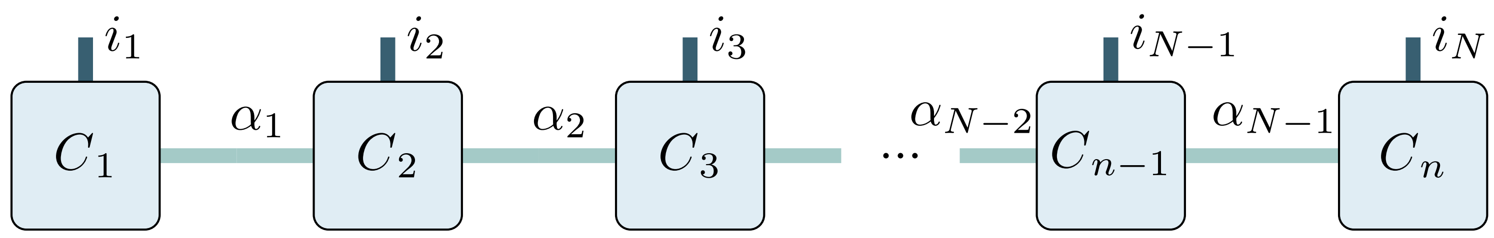
$$\left|\Psi(t)\right\rangle = \sum_{i_1 i_2 \ldots i_N} C(i_1, i_2, \ldots, i_N; t)\left|i_1\right\rangle \otimes \left|i_2\right\rangle \cdots \left|i_N\right\rangle$$

$$C(i_1, \ldots, i_N) \approx C_1(i_1)C_2(i_2)\cdots C_N(i_N)$$

The **cores** $C_k(i_k)$ are $(r_{k-1} \times r_k)$ complex matrices

r_k are called **compression ranks**

$$|\Psi(t)\rangle =$$



Tensor Trains / Matrix Product States

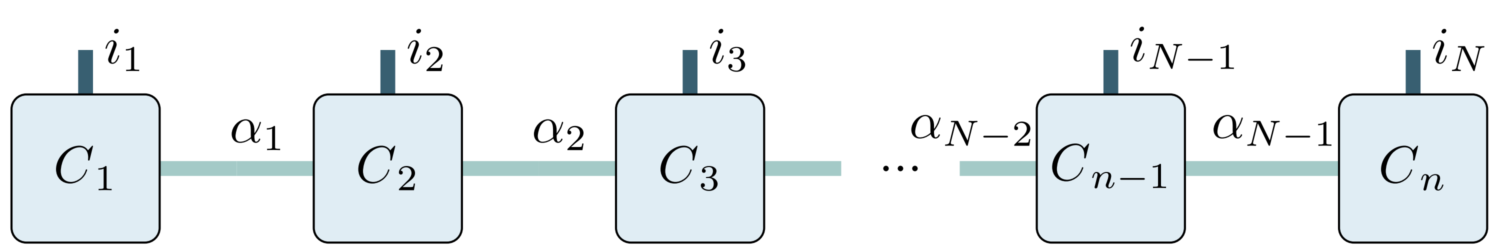
$$\left|\Psi(t)\right\rangle = \sum_{i_1 i_2 \dots i_N} C(i_1, i_2, \dots, i_N; t)\left|i_1\right\rangle \otimes \left|i_2\right\rangle \cdots \left|i_N\right\rangle \quad p^N$$

$$\boxed{C(i_1, \dots, i_N) \approx C_1(i_1) C_2(i_2) \cdots C_N(i_N)} \quad Npr^2$$

The **cores** $C_k(i_k)$ are $(r_{k-1} \times r_k)$ complex matrices

r_k are called **compression ranks**

$|\Psi(t)\rangle =$



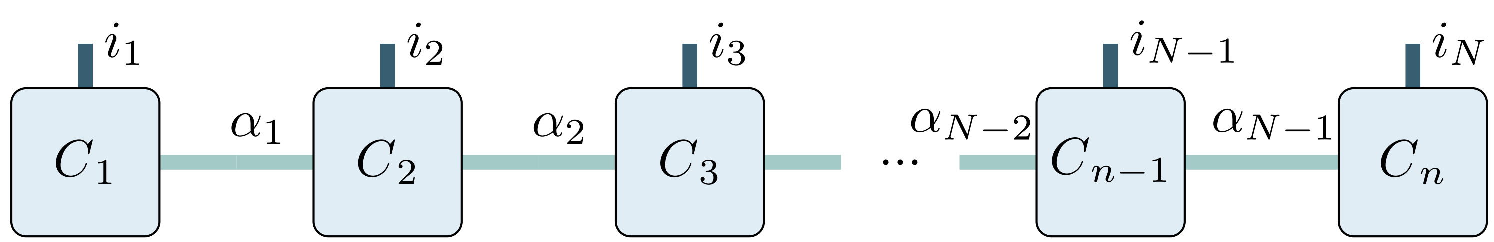
Tensor Trains / Matrix Product States

$$|\Psi(t)\rangle = \sum_{i_1 i_2 \dots i_N} C(i_1, i_2, ..., i_N; t)|i_1\rangle \otimes |i_2\rangle \cdots |i_N\rangle \quad p^N$$

$$C(i_1, ..., i_N) \approx C_1(i_1)C_2(i_2)\cdots C_N(i_N) \quad Npr^2$$

The **cores** $C_k(i_k)$ are $(r_{k-1} \times r_k)$ complex matrices

r_k are called **compression ranks**

$|\Psi(t)\rangle =$ 

Tensor Trains / Matrix Product States

$$|\Psi(t)\rangle = \sum_{i_1 i_2 \dots i_N} C(i_1, i_2, \dots, i_N; t)|i_1\rangle \otimes |i_2\rangle \cdots |i_N\rangle \quad p^N$$

$$C(i_1, \dots, i_N) \approx C_1(i_1)C_2(i_2)\cdots C_N(i_N) \quad Npr^2$$

The **cores** $C_k(i_k)$ are $(r_{k-1} \times r_k)$ complex matrices

r_k are called **compression ranks**

Low rank dynamical approximations.
Effective if r is small.

Tensor Trains / Matrix Product States

$$\left|\Psi(t)\right\rangle = \sum_{i_1\cdots i_N} C_1(i_1,t)C_2(i_2,t)\cdots C_N(i_N,t)\left|i_1\right\rangle \otimes \left|i_2\right\rangle\cdots\left|i_N\right\rangle.$$

TT/MPS do not form a vector space

1) Time Evolving Block Decimation (Vidal 2003)

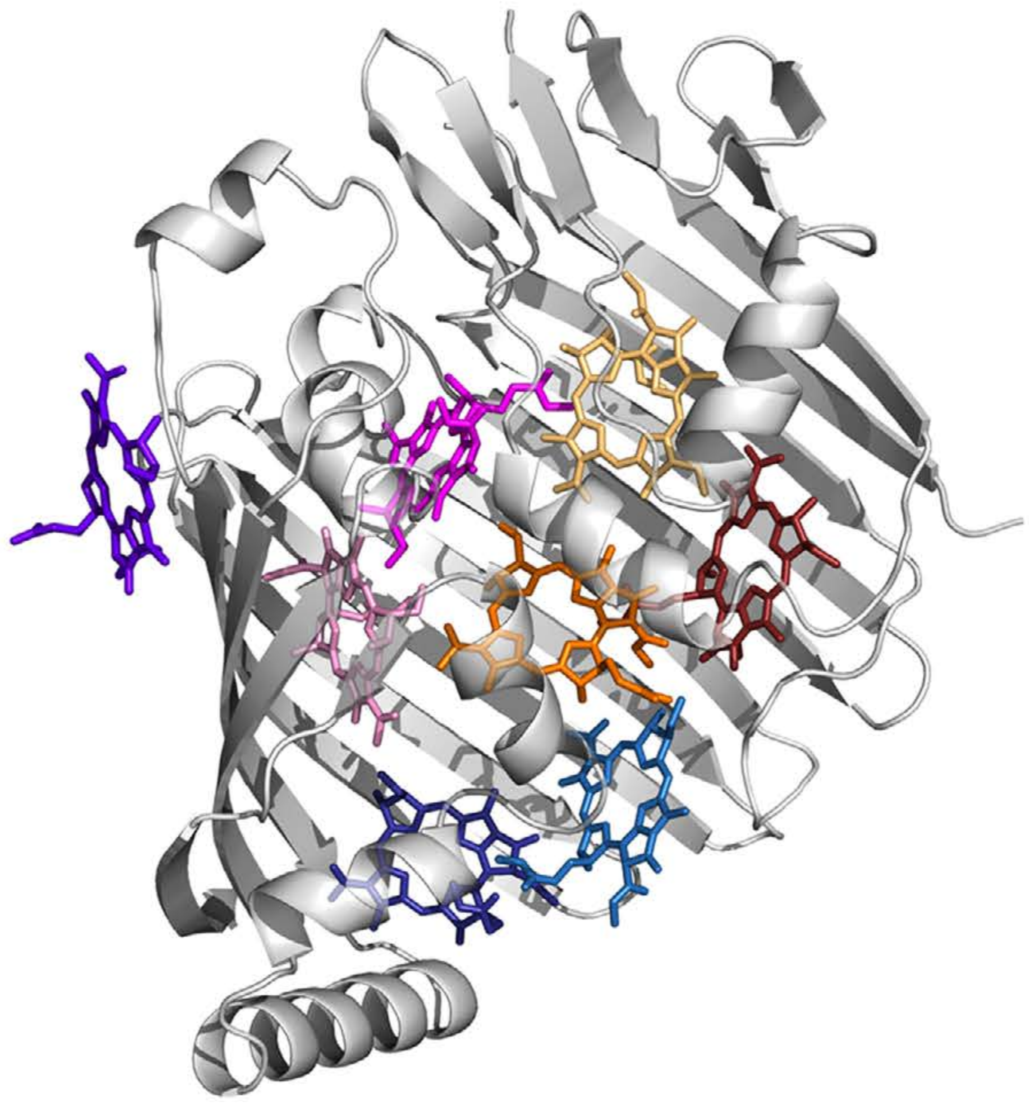
2) Time dependent Variational Principle (Osborne 2013, Lubich, Oseledets, 2015)

$$\frac{d}{dt}\left|\Psi(C(t))\right\rangle = -i\hat{P}_{\mathcal{T}(C(t))}H\left|\Psi(C(t))\right\rangle$$

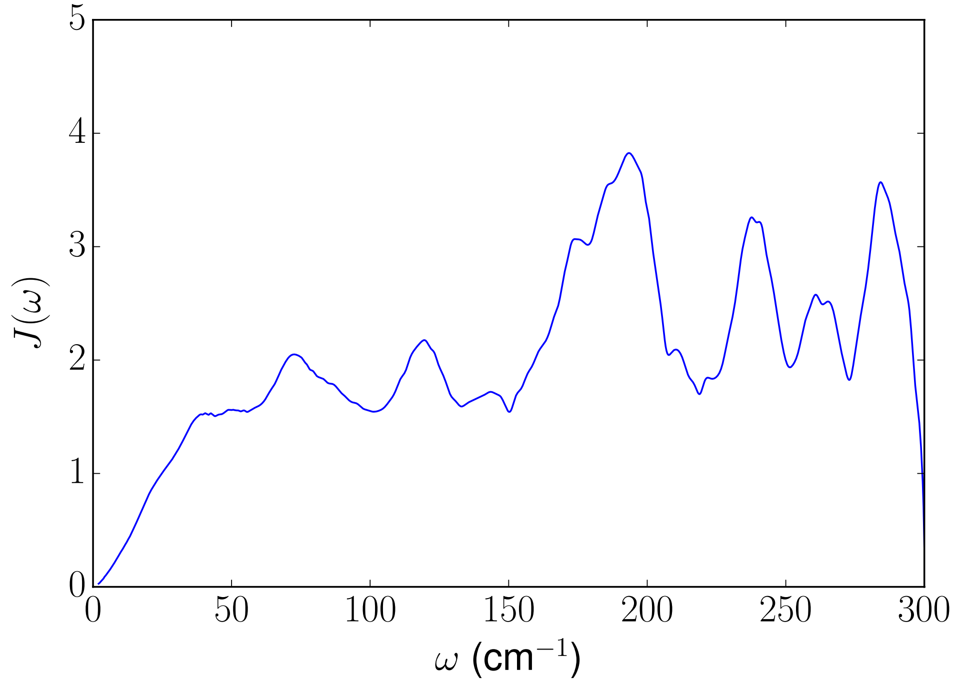
1) Oseledets SIAM J Num Anal (2011)
2) Lubich et al. SIAM J Num Anal (2015)
3) Borrelli, R. and Gelin, M. *J Chem Phys* (2016)

Exciton Dynamics in the Fenna-Matthews-Olson Complex

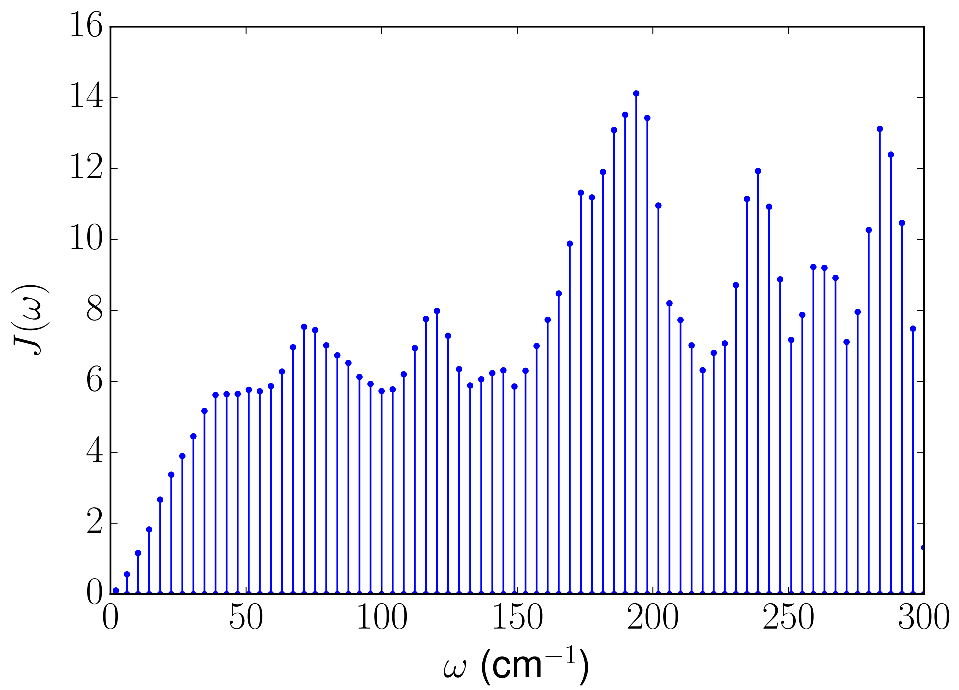
$$74 \quad \text{vibrations per site} = 518 + \widetilde{518}$$
$$1036 \text{ vib}$$



Experimental



Discretization



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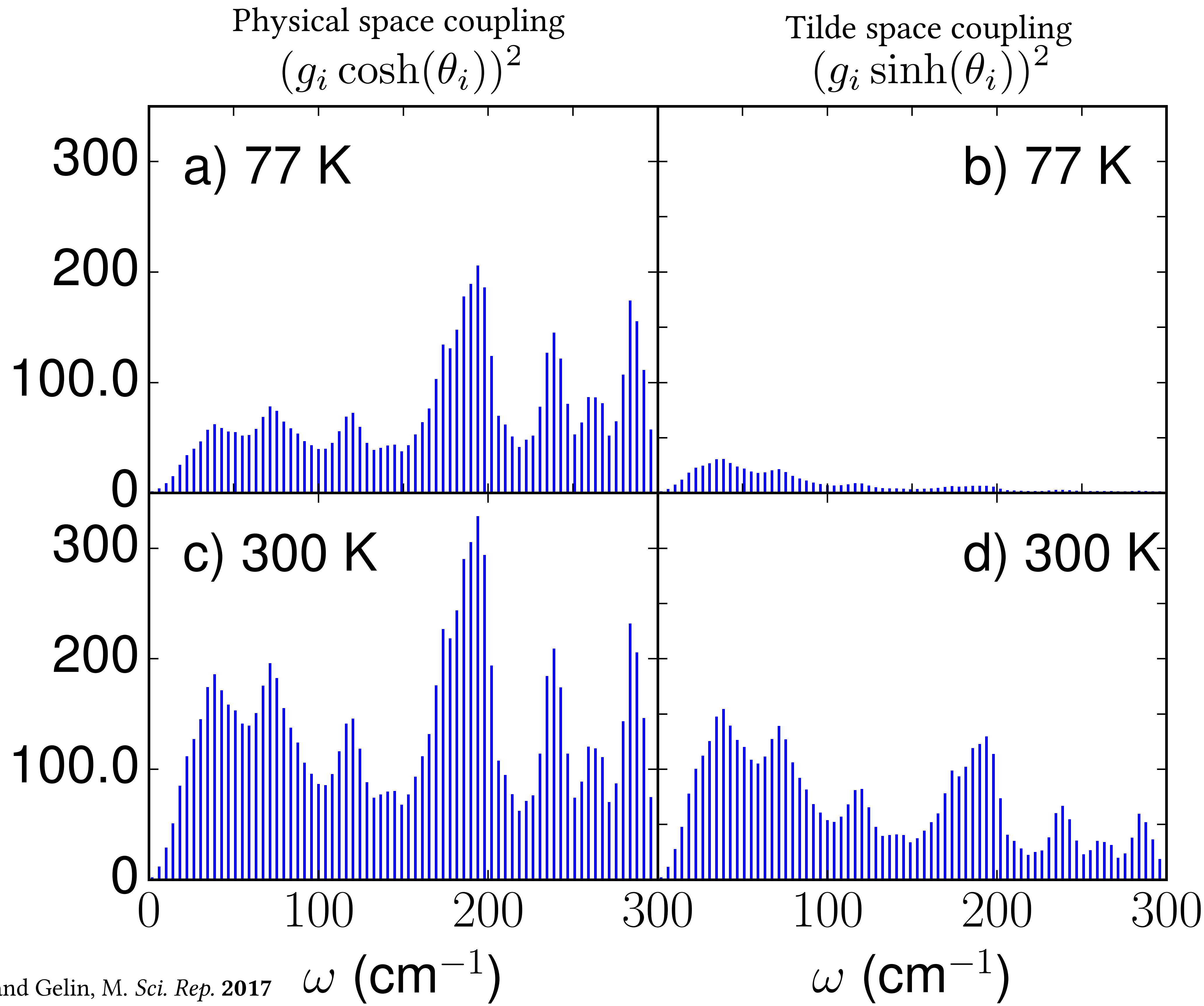
Exciton Dynamics in the Fenna-Matthews-Olson Complex



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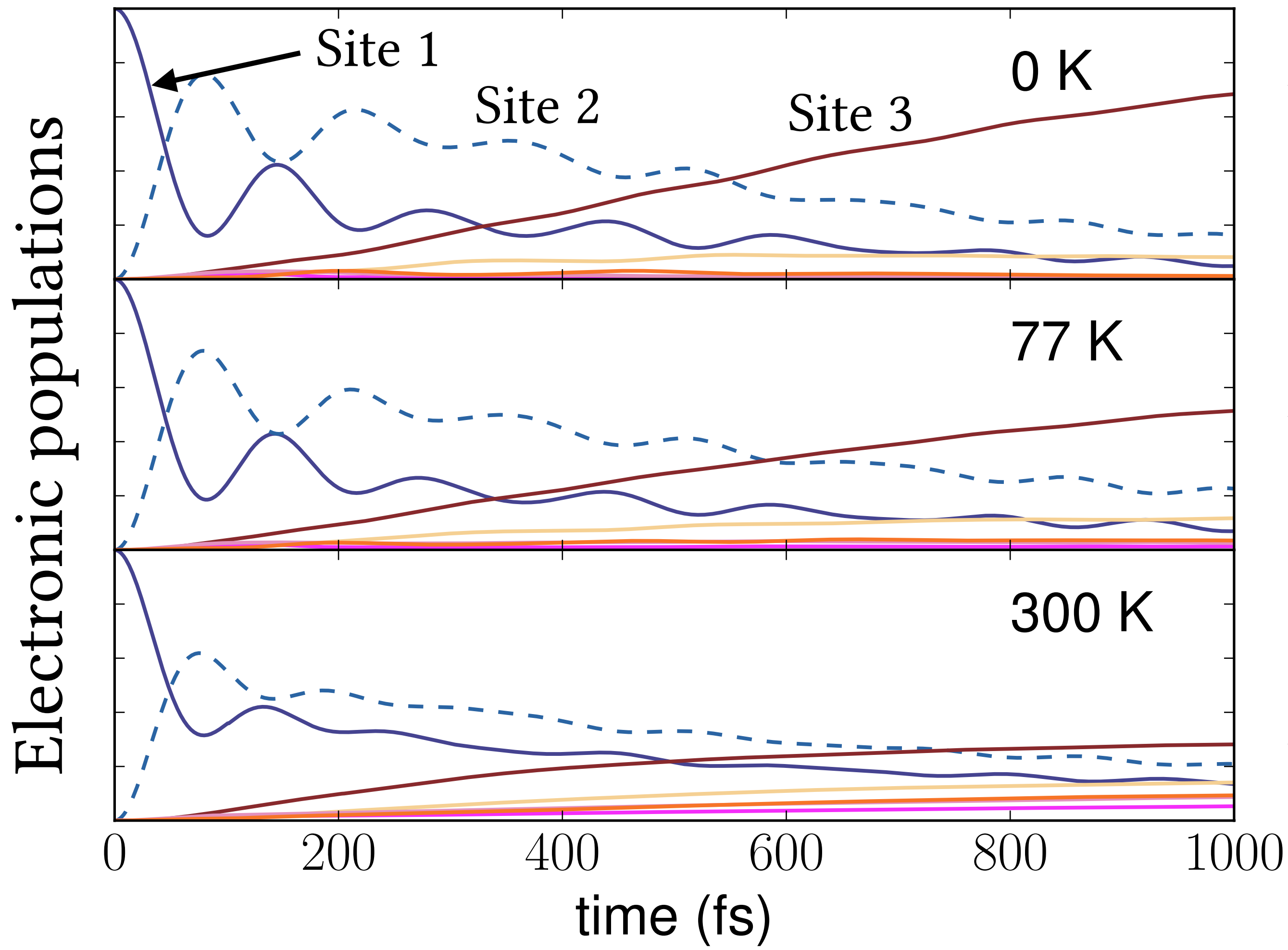
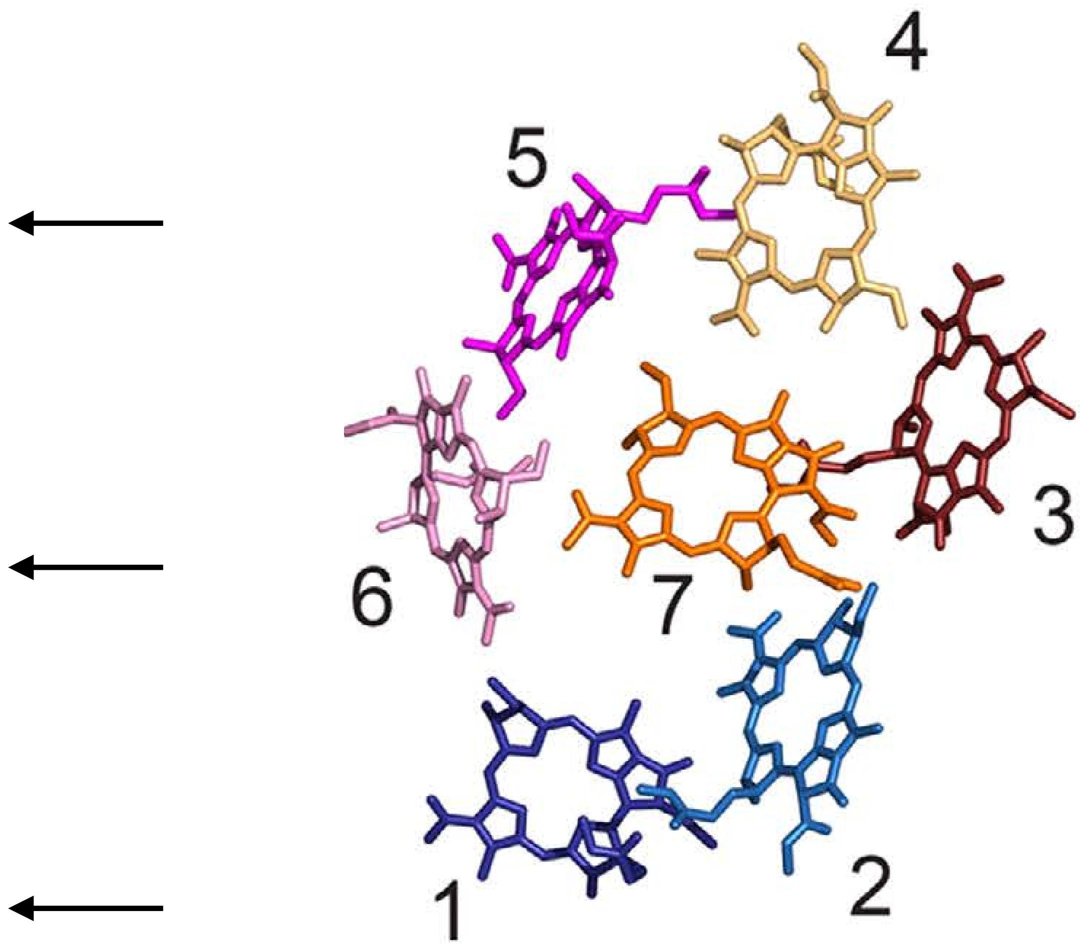
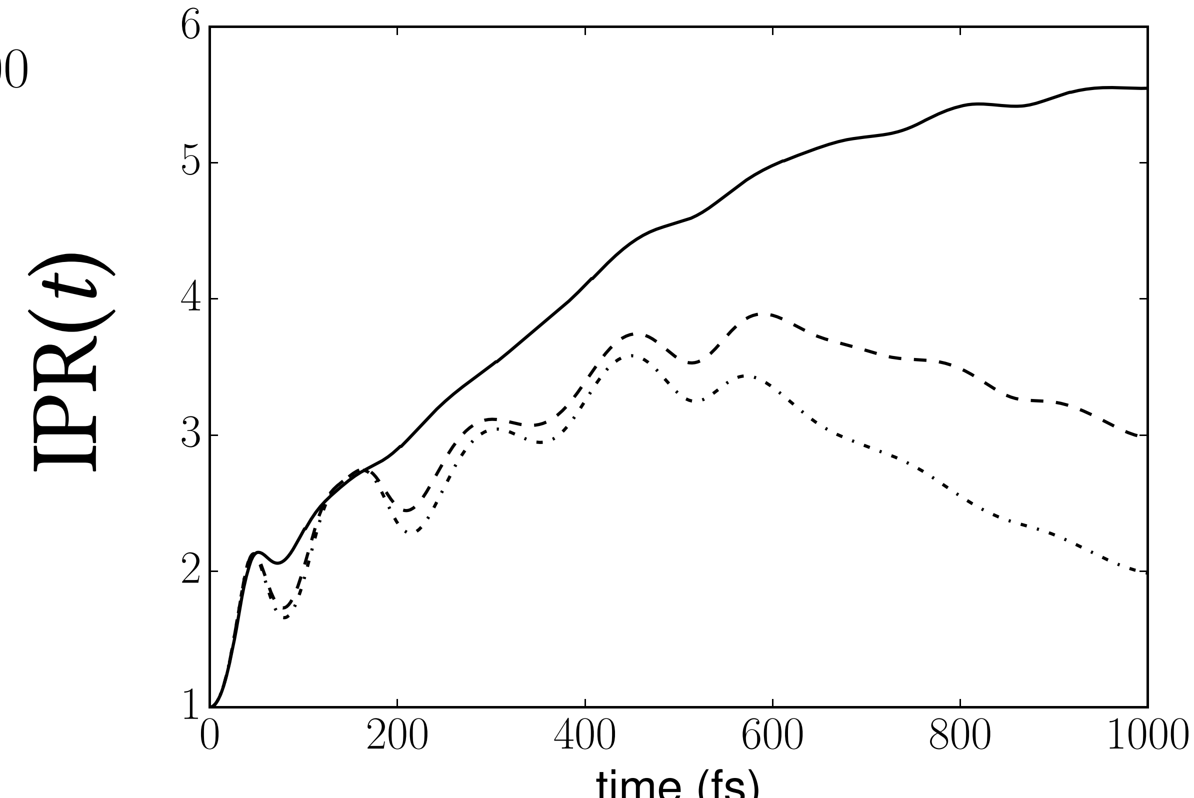
Exciton Dynamics in the Fenna-Matthews-Olson Complex



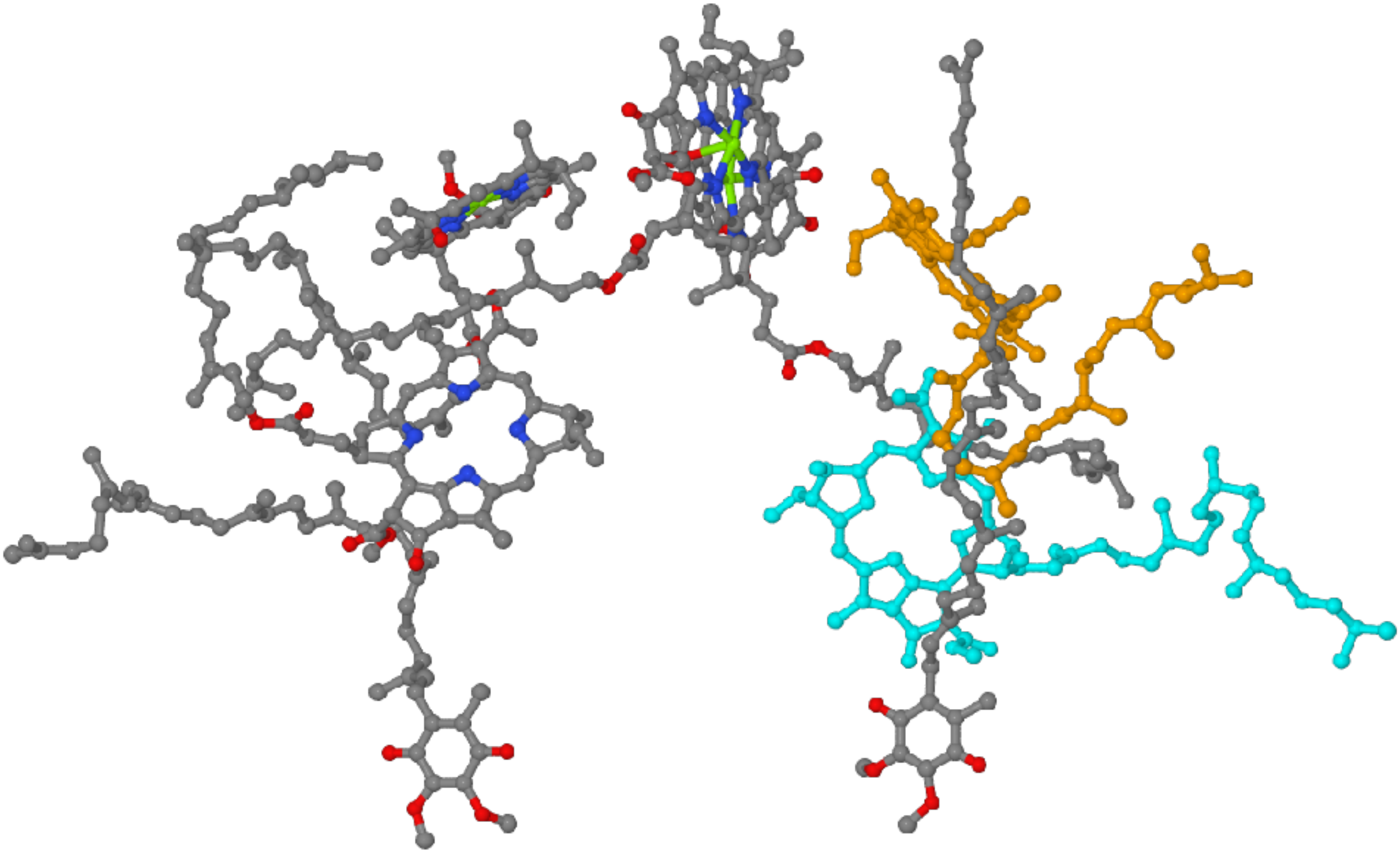


Converged calculations ranks r=60.

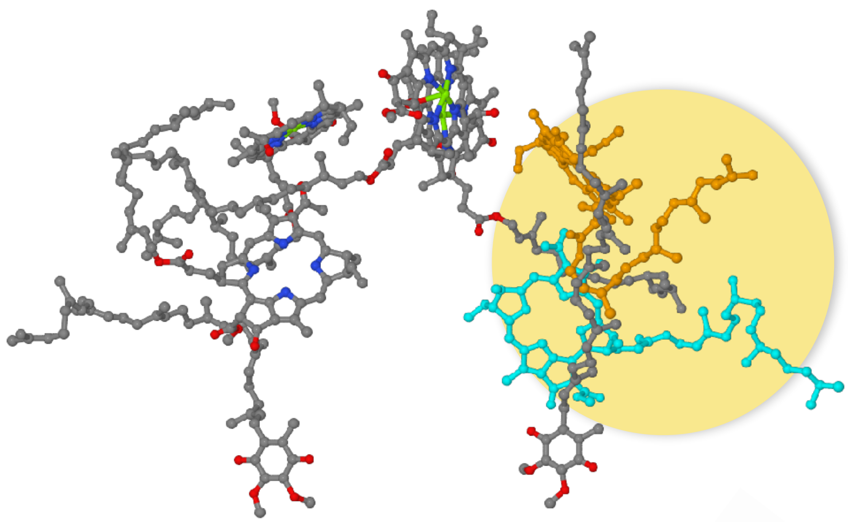


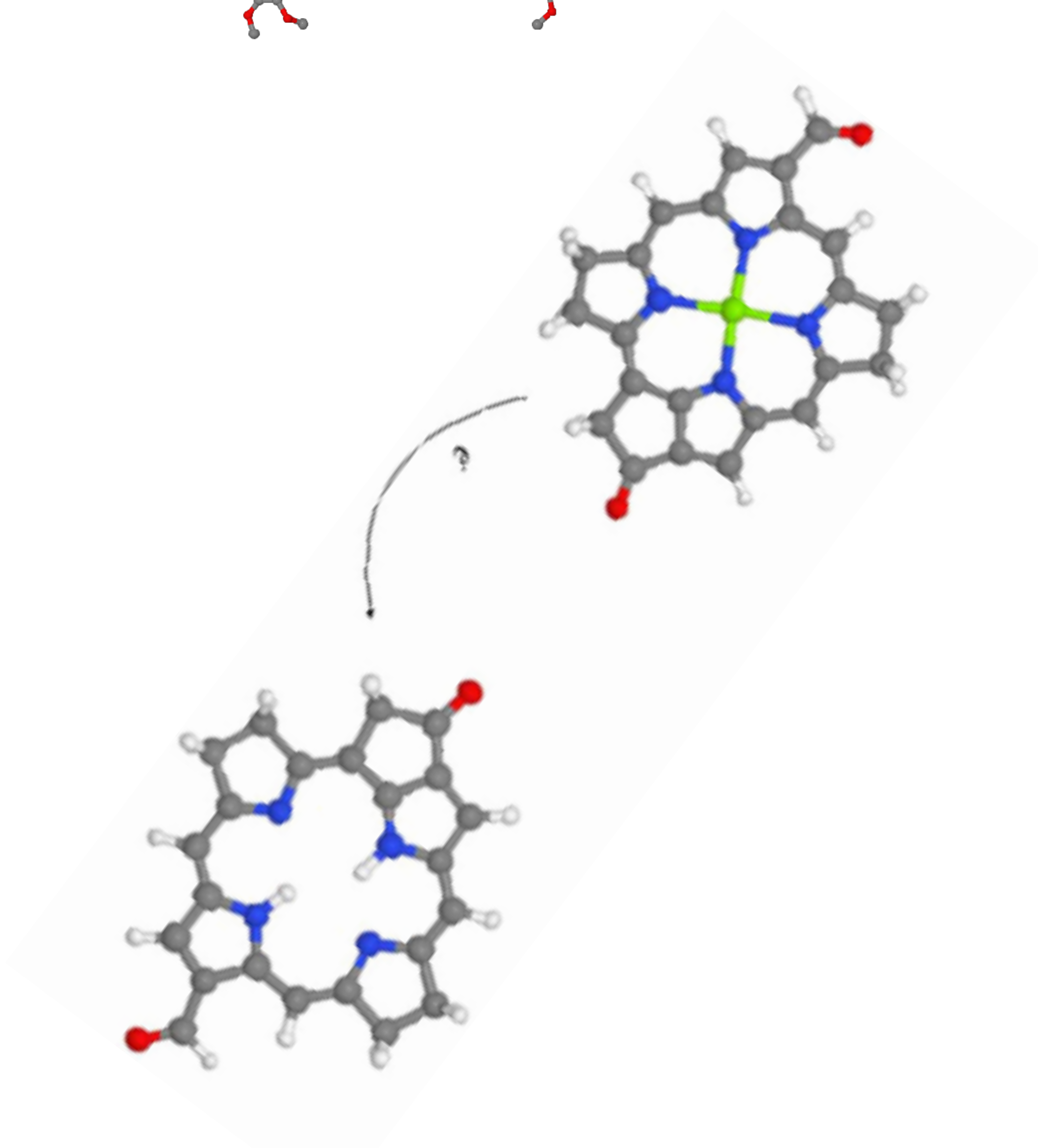
IPR clearly shows the delocalization process at high temperature

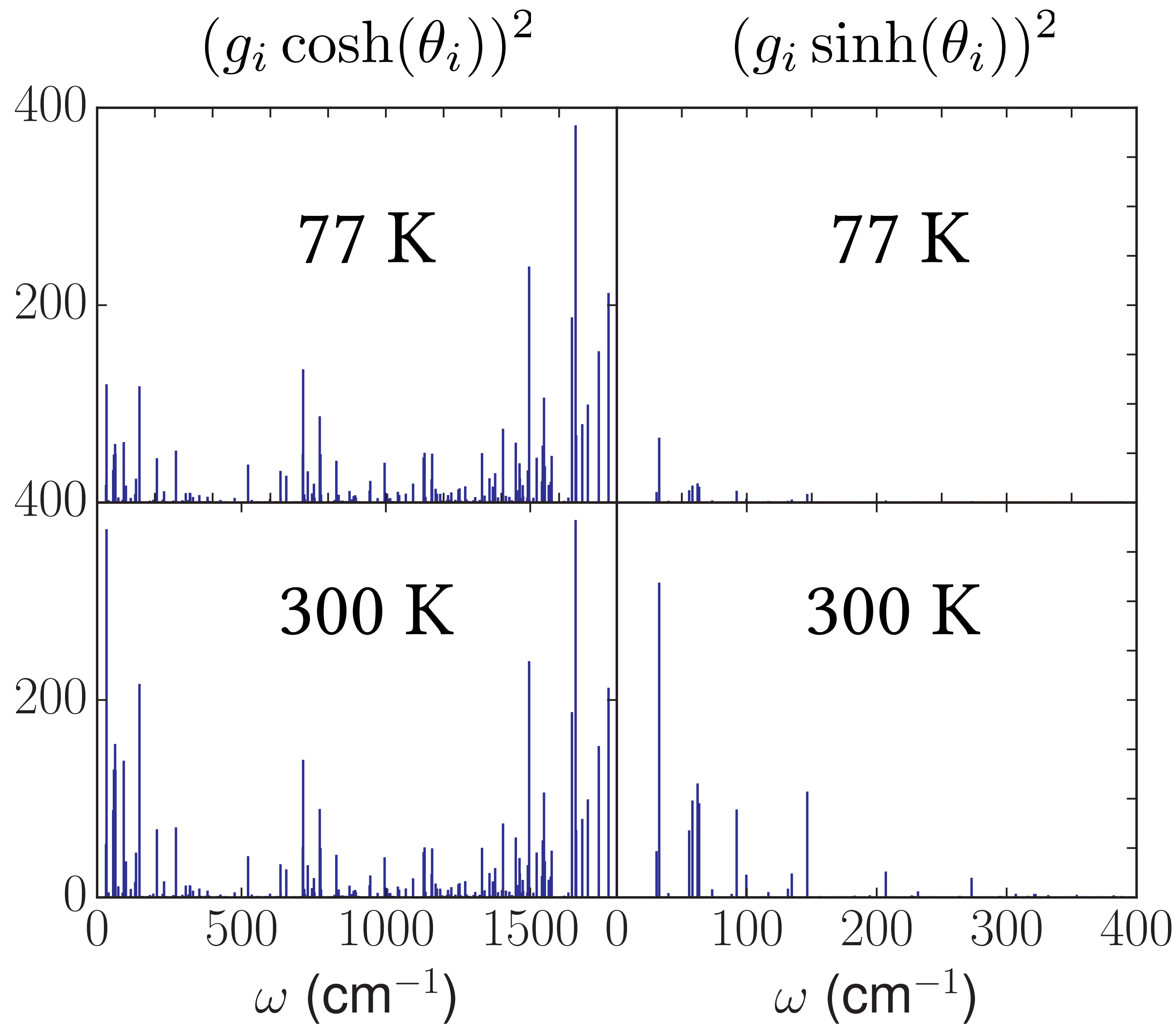
Electron Transfer Dynamics in RC



Electron Transfer Dynamics in RC







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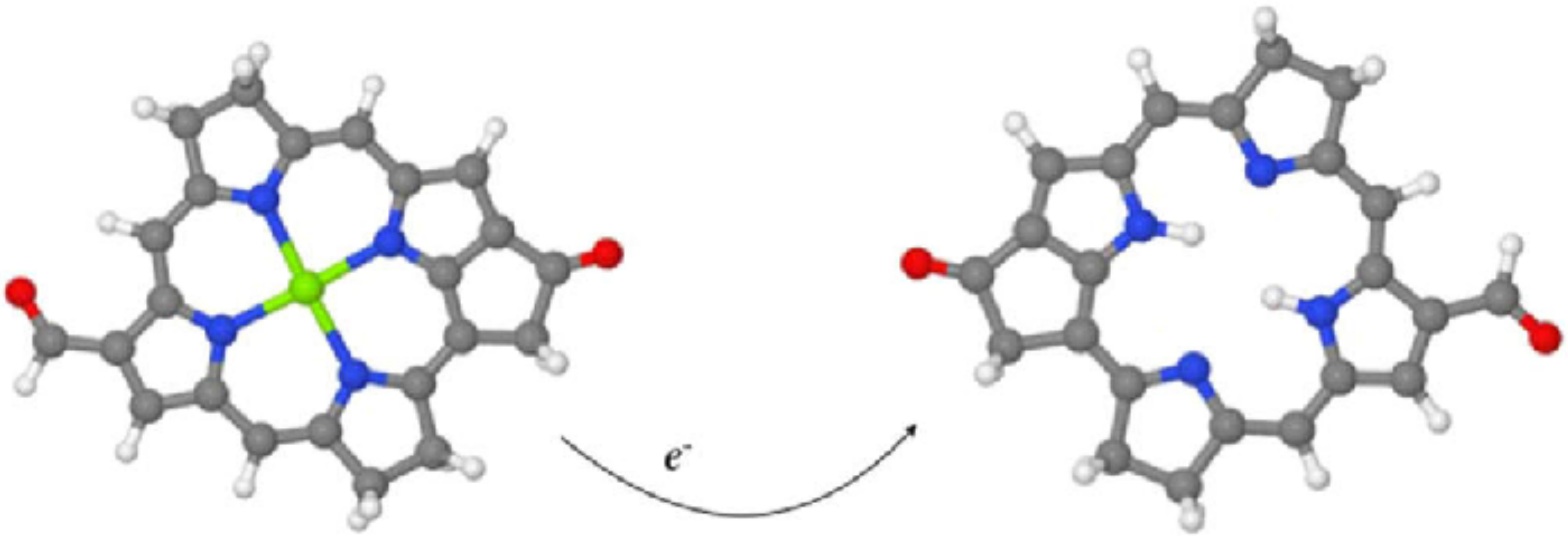
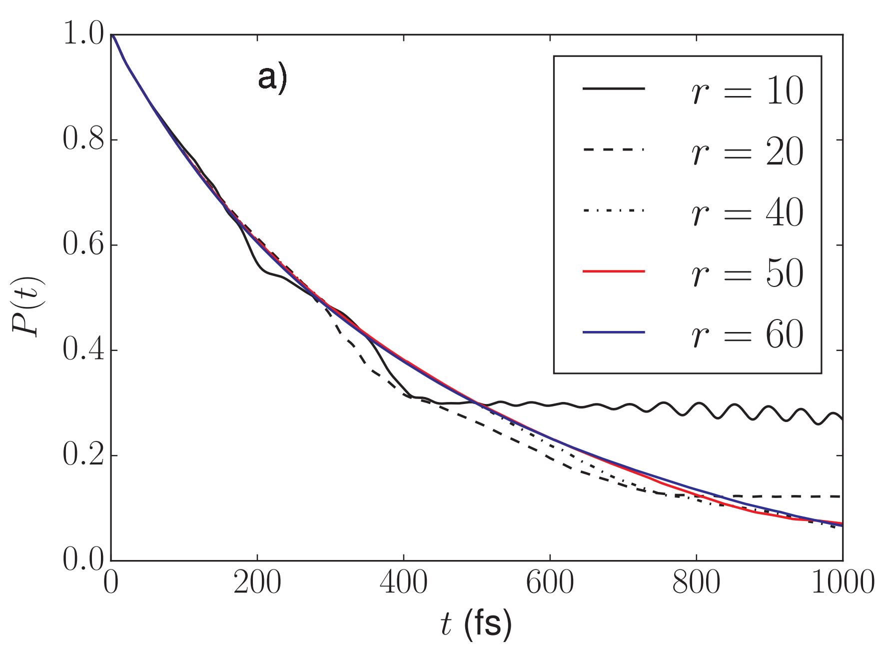
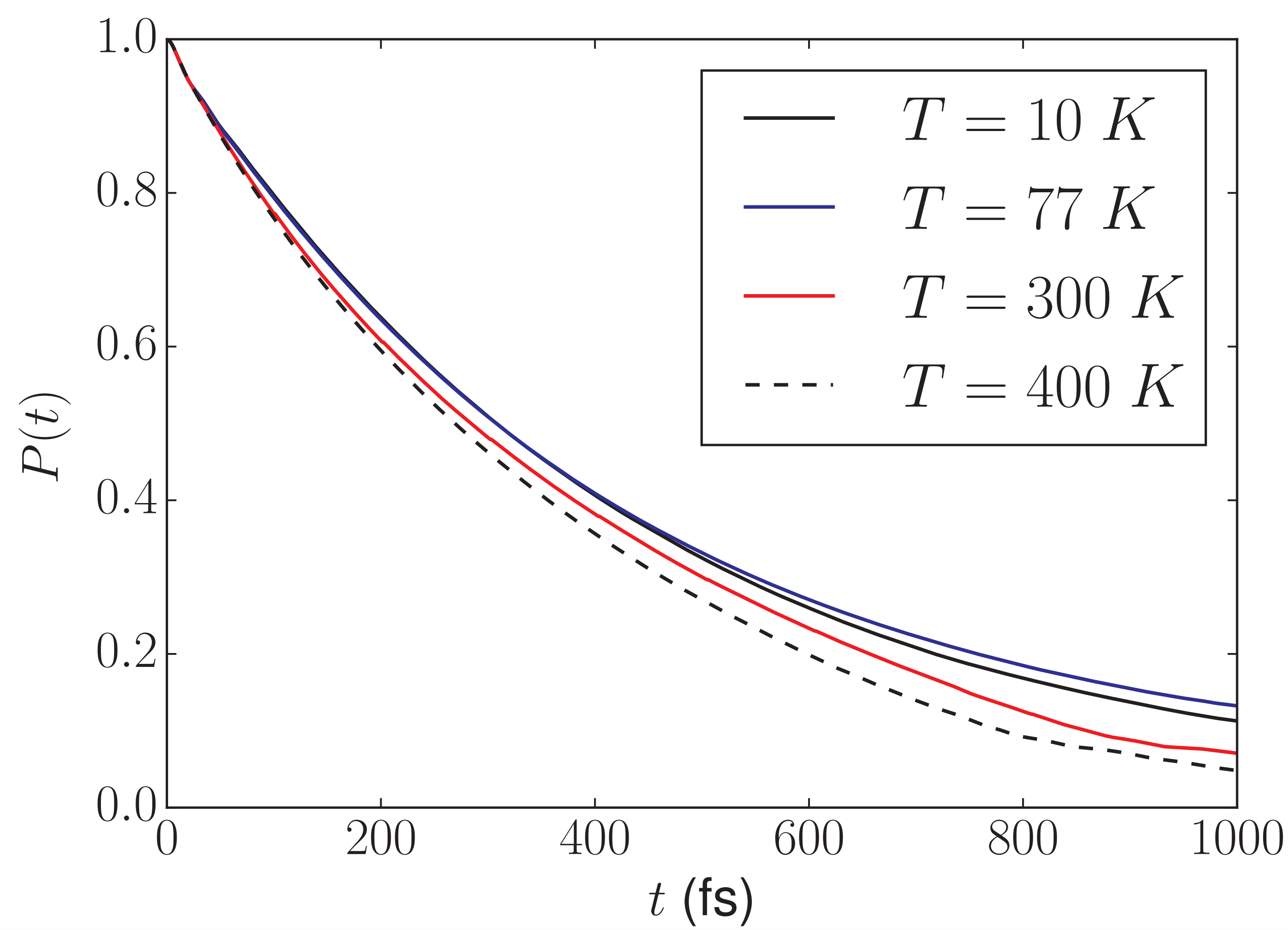
Electron Transfer Dynamics in RC







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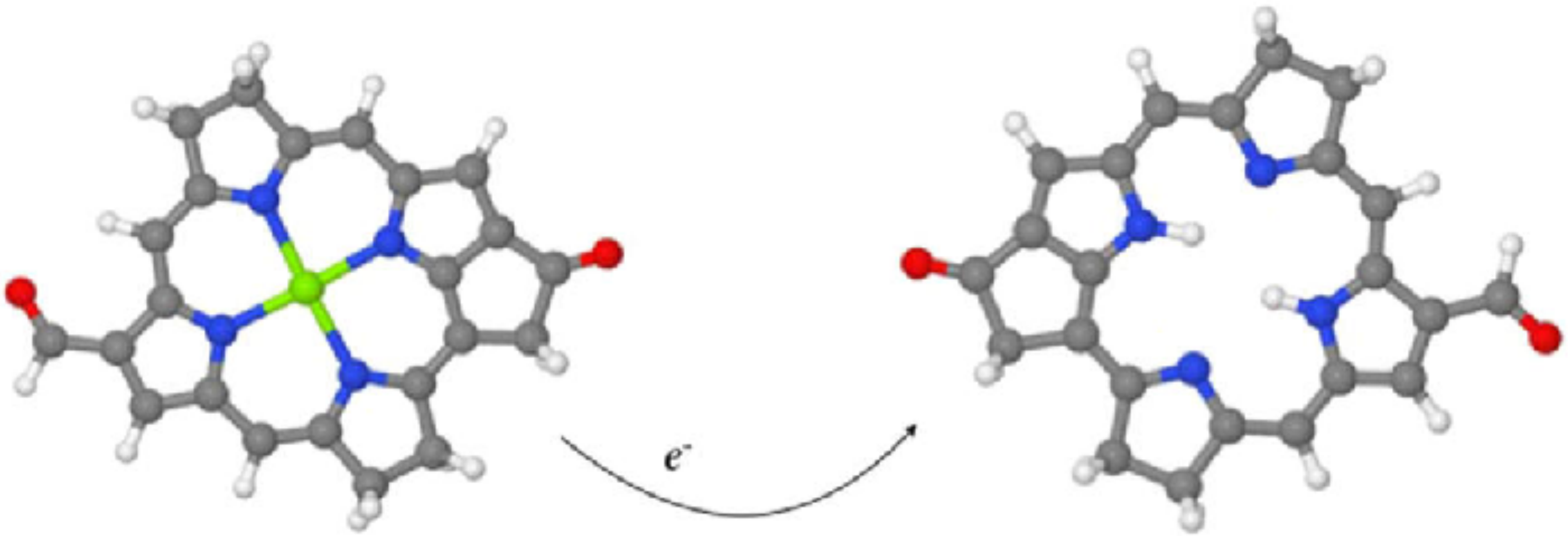
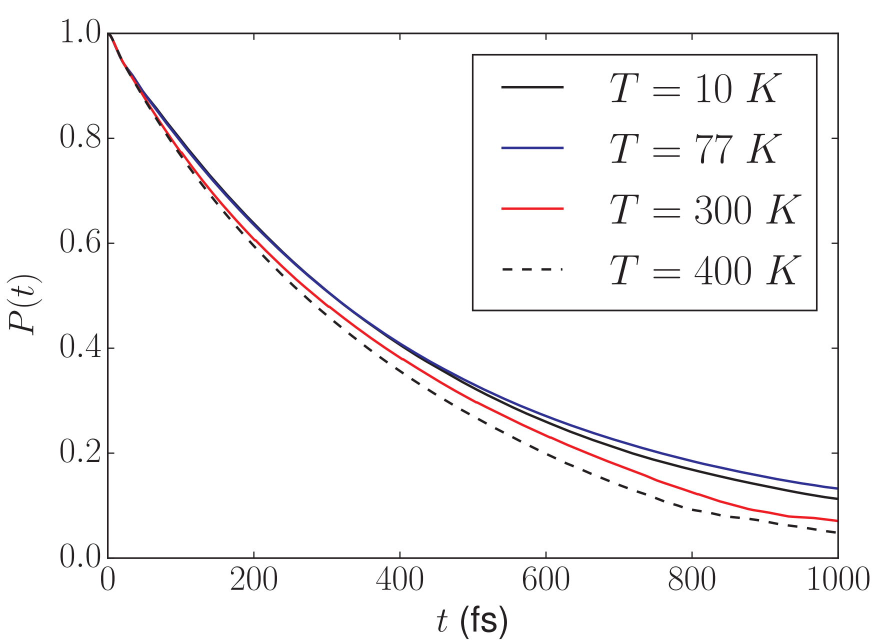
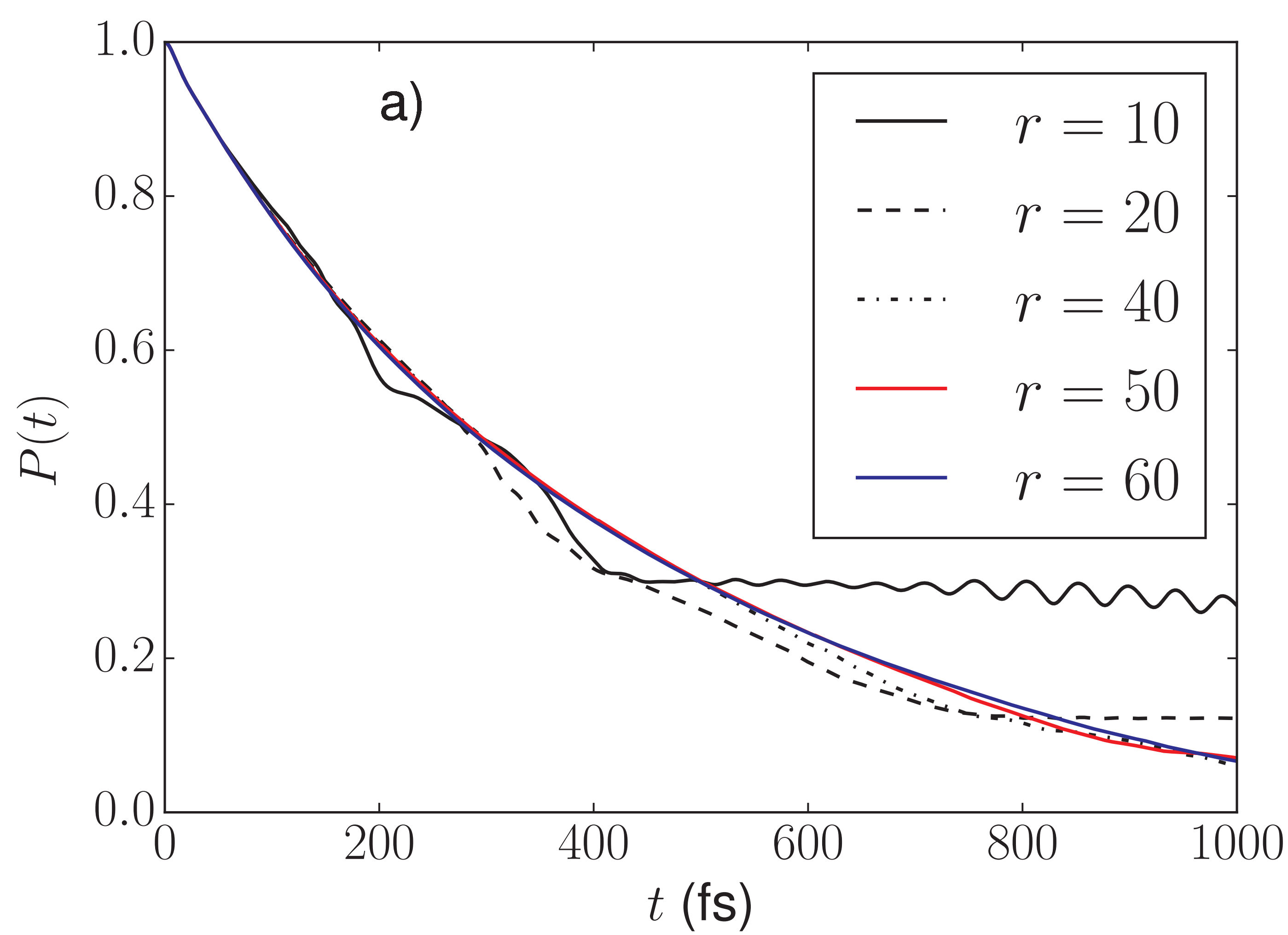
Electron Transfer Dynamics in RC







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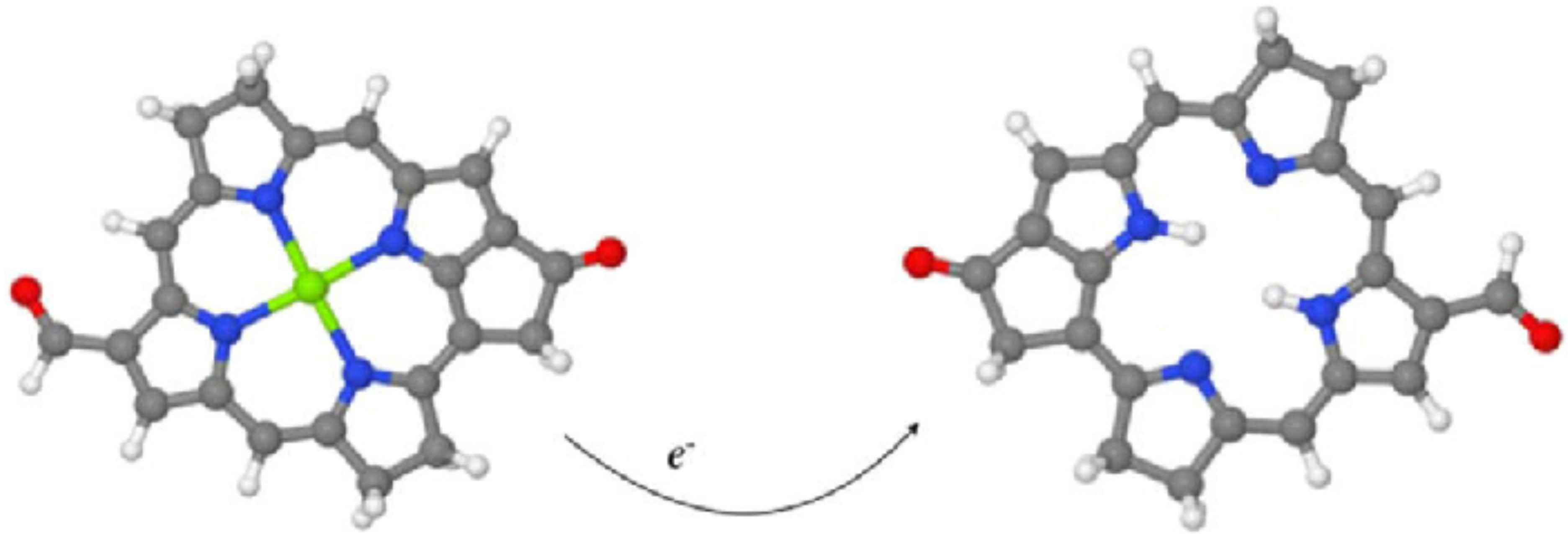
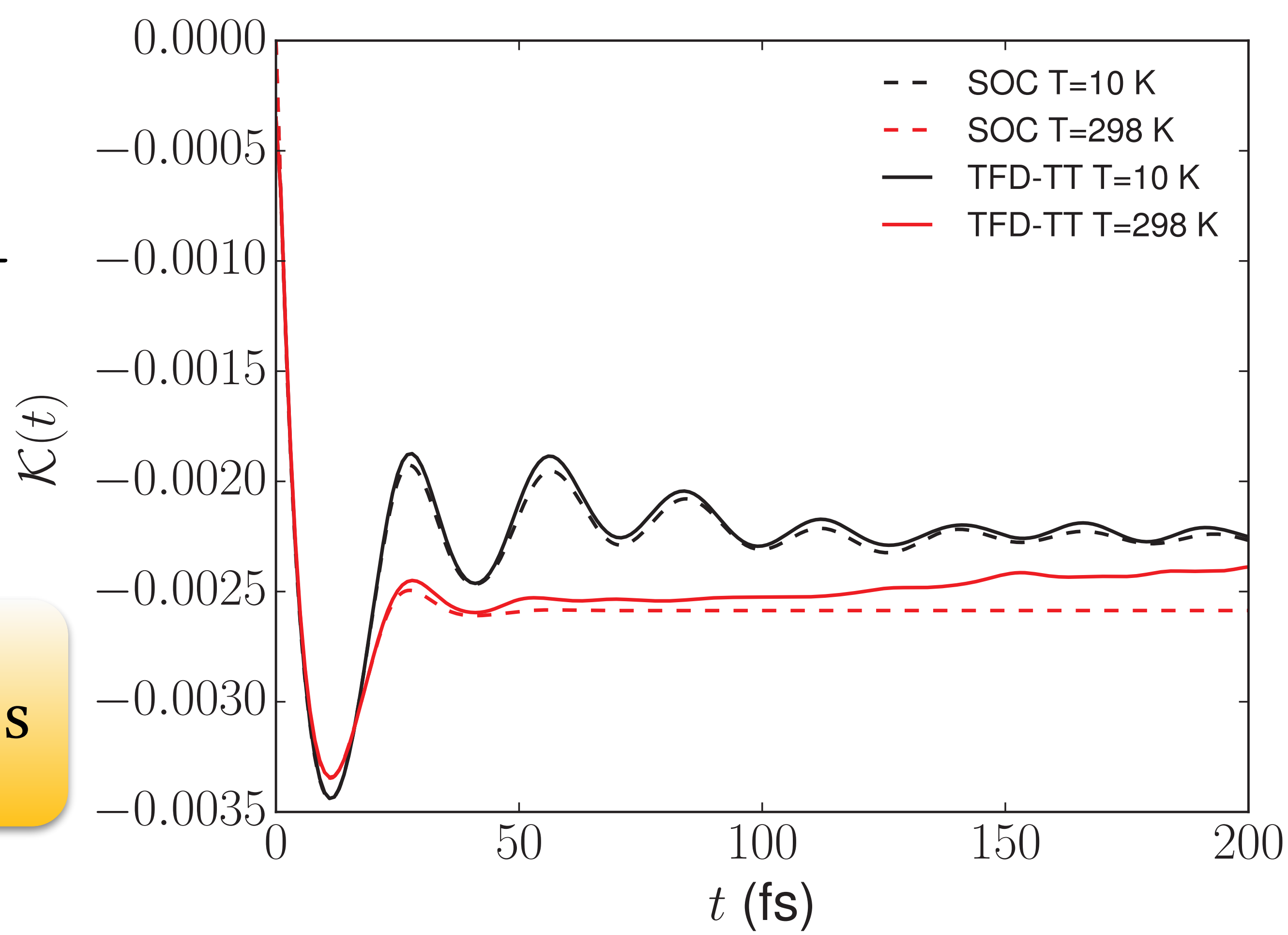
Electron Transfer Dynamics in RC



$$\mathcal{K}_2(t) = \mathcal{N}\int_0^t \mathrm{Tr}(e^{iH_A(\tau+i\beta)}e^{-iH_F\tau})d\tau$$

$$\mathcal{K}(t) = \dot{P}_A(t)/P_A(t)$$



Short time dynamics to extract rates

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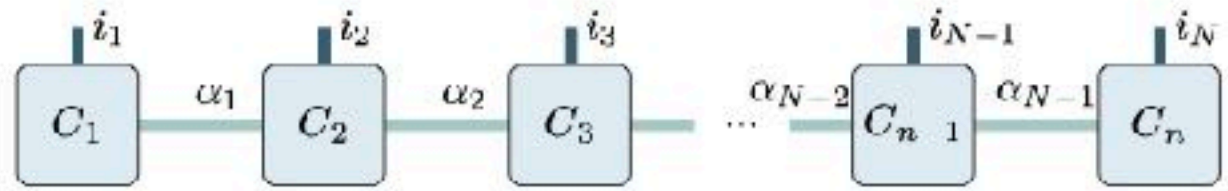
Non-Linear Spectroscopic signals

$$|\psi(t)\rangle = e^{-i\bar{H}_\theta t}|\psi\rangle$$



Four-time correlation functions

$$\Phi(\tau_4, \tau_3, \tau_2, \tau_1) = \left\langle \hat{\mu}(\tau_4)\hat{\mu}(\tau_3)\hat{\mu}(\tau_2)\hat{\mu}(\tau_1) \right\rangle$$

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Non-Linear Spectroscopic signals

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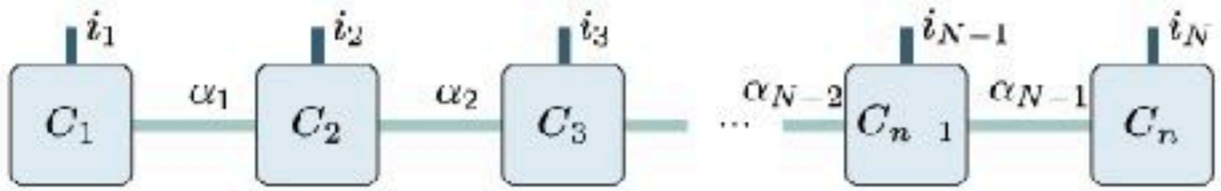

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Third-order response functions at finite temperature

$$R_1^s(t_3, t_2, t_1) = \langle \psi(t_2) | BU^\dagger(t_3) | \psi(t_1 + t_2 + t_3) \rangle$$

$$B = \hat{\mu}_+\hat{\mu}_- = |e\rangle\langle e| \qquad U(t) = e^{-iH_\theta^v t}$$

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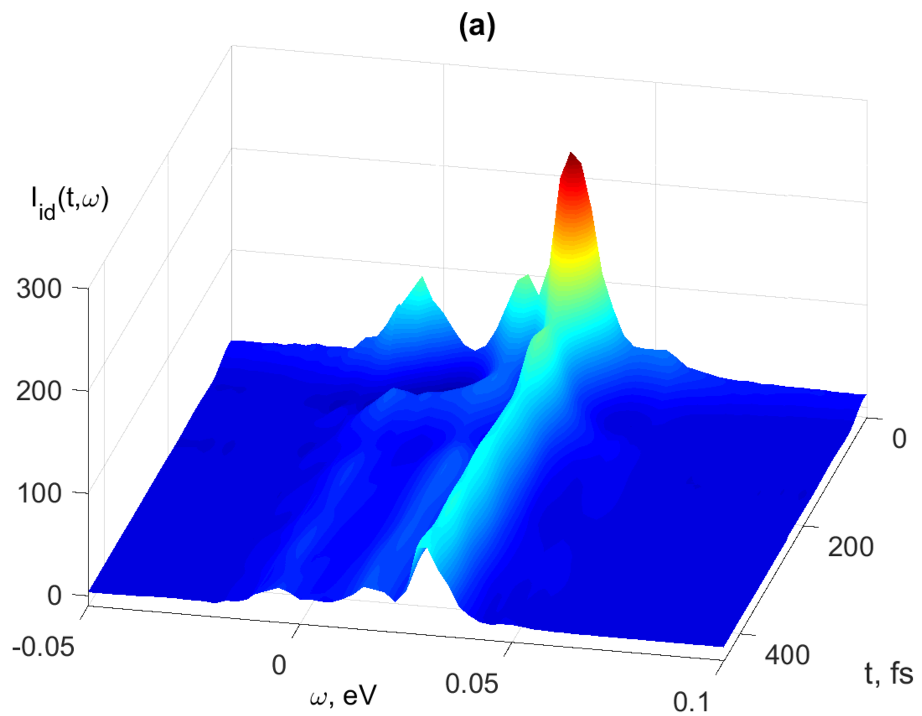
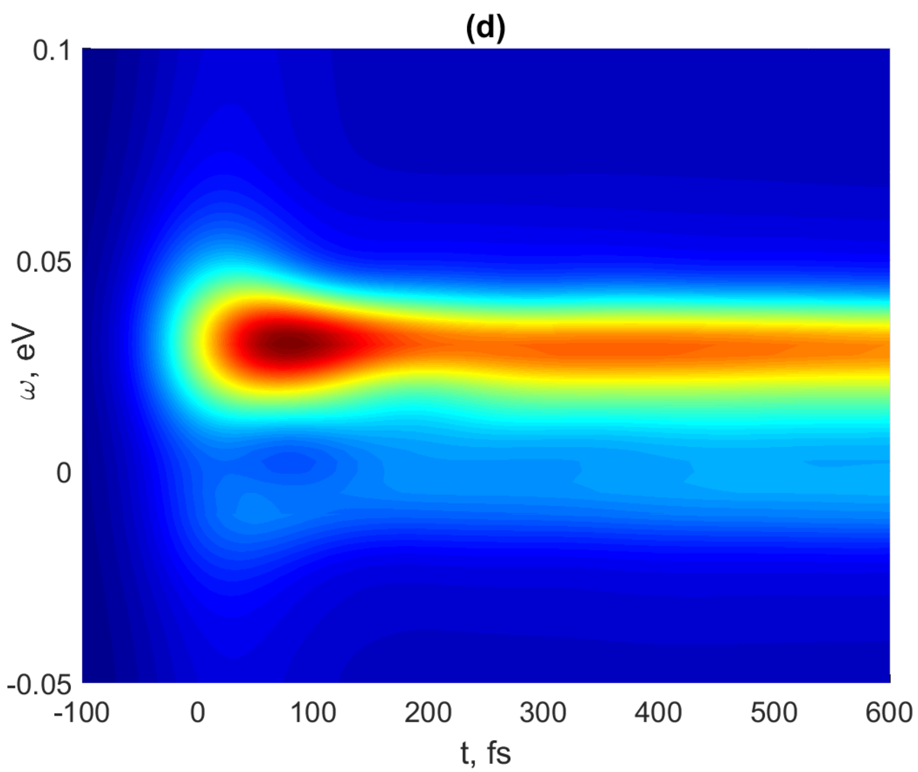
Time-Resolved Fluorescence of FMO

$$I(t,\omega) \sim \mathrm{Re} \int_{-\infty}^{\infty} dt' \int_0^{\infty} dt_3 \int_0^{\infty} dt_2 \int_0^{\infty} dt_1 \mathscr{E}_g(t'-t)\mathscr{E}_g(t'-t_3-t)\mathscr{E}_p(t'-t_3-t_2)\mathscr{E}_p(t'-t_3-t_2-t_1)$$

$$\times\, e^{-(\gamma-i\omega)t_3} \left\{R_1^s(t_3,t_2,t_1)e^{i\omega_p t_1} + R_2^s(t_3,t_2,t_1)e^{-i\omega_p t_1}\right\}$$





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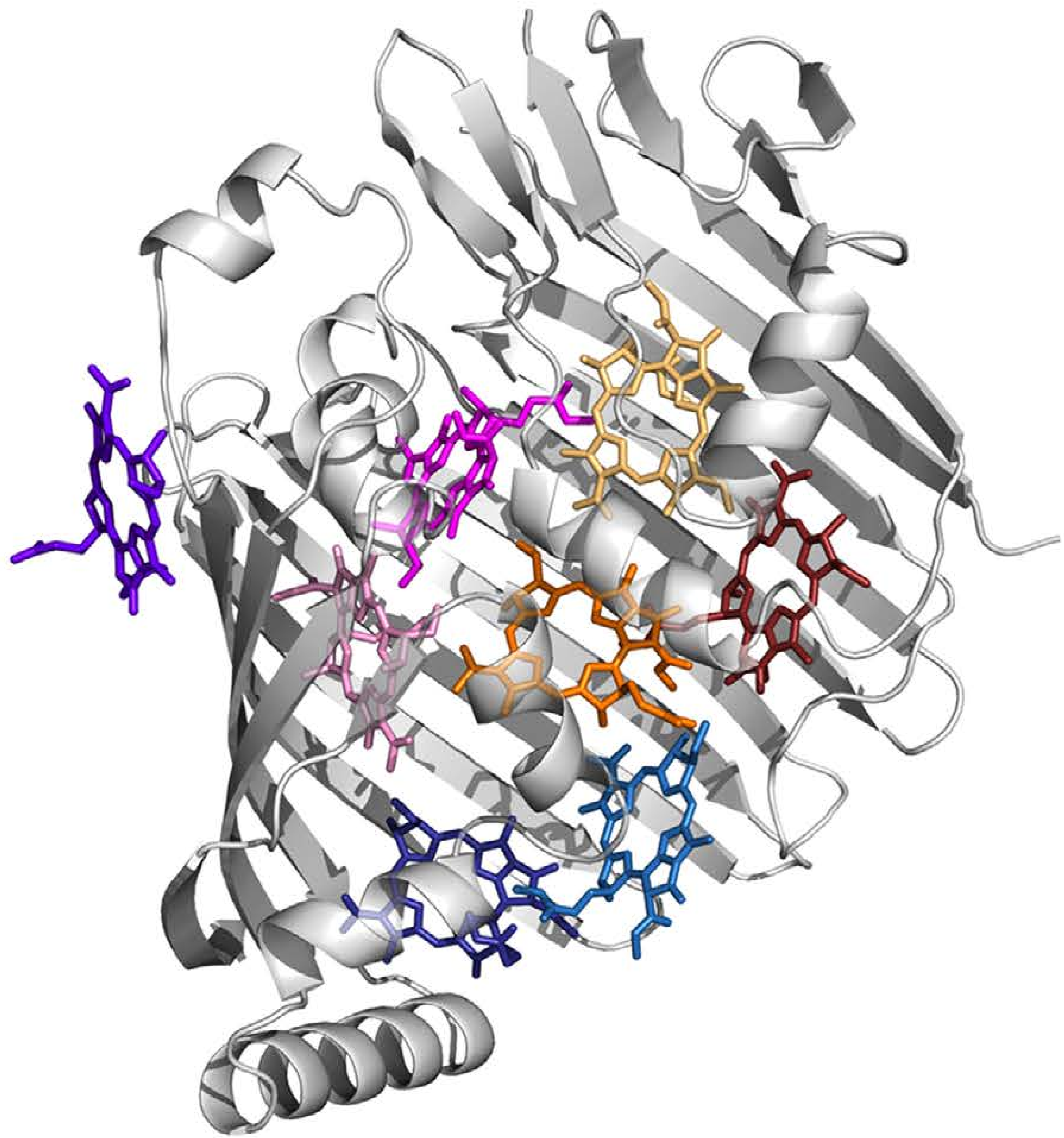
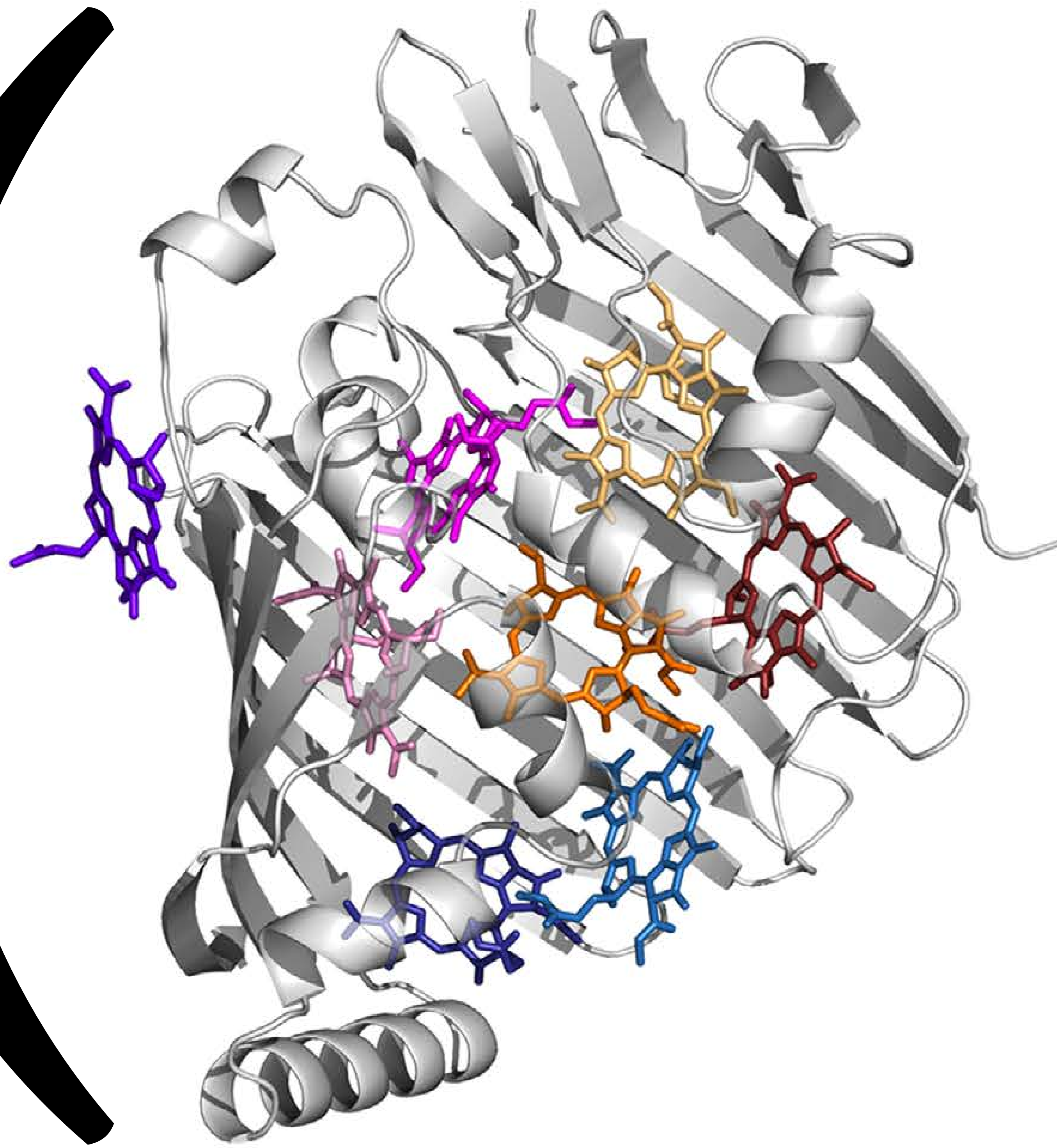
Reduced Density Matrix Formalism

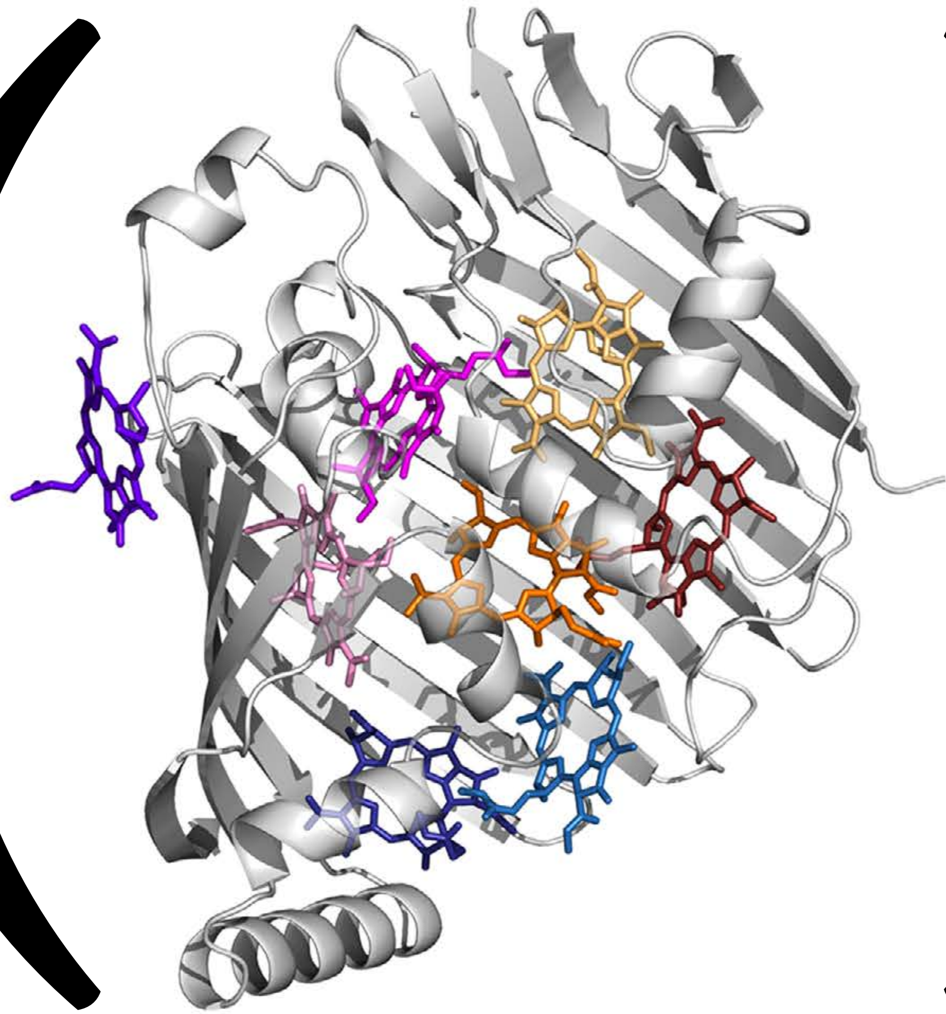


Reduced Density Matrix Formalism

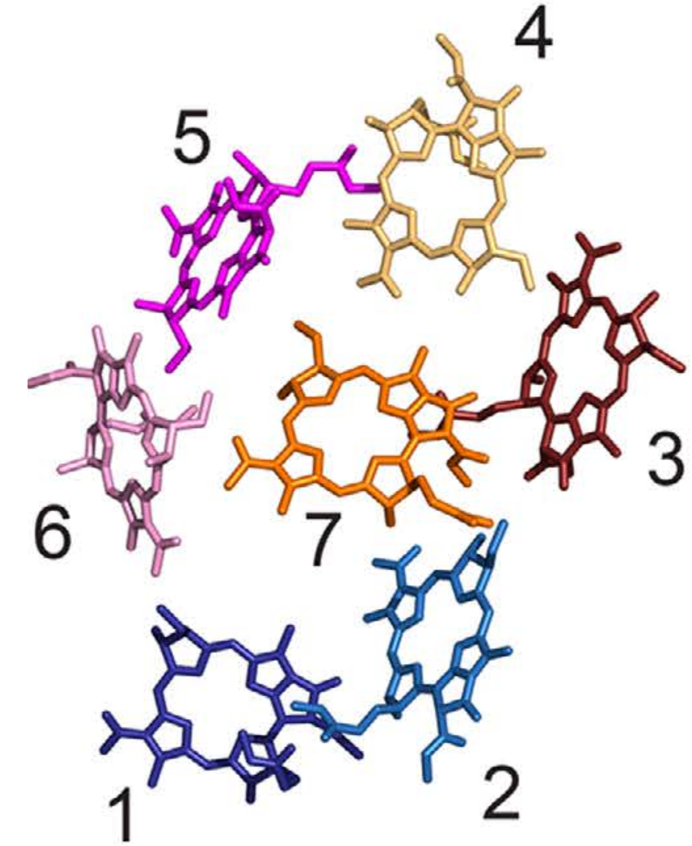
$\mathrm{Tr}_B \Big($  $\Big)$

Reduced Density Matrix Formalism

Tr_{B} (

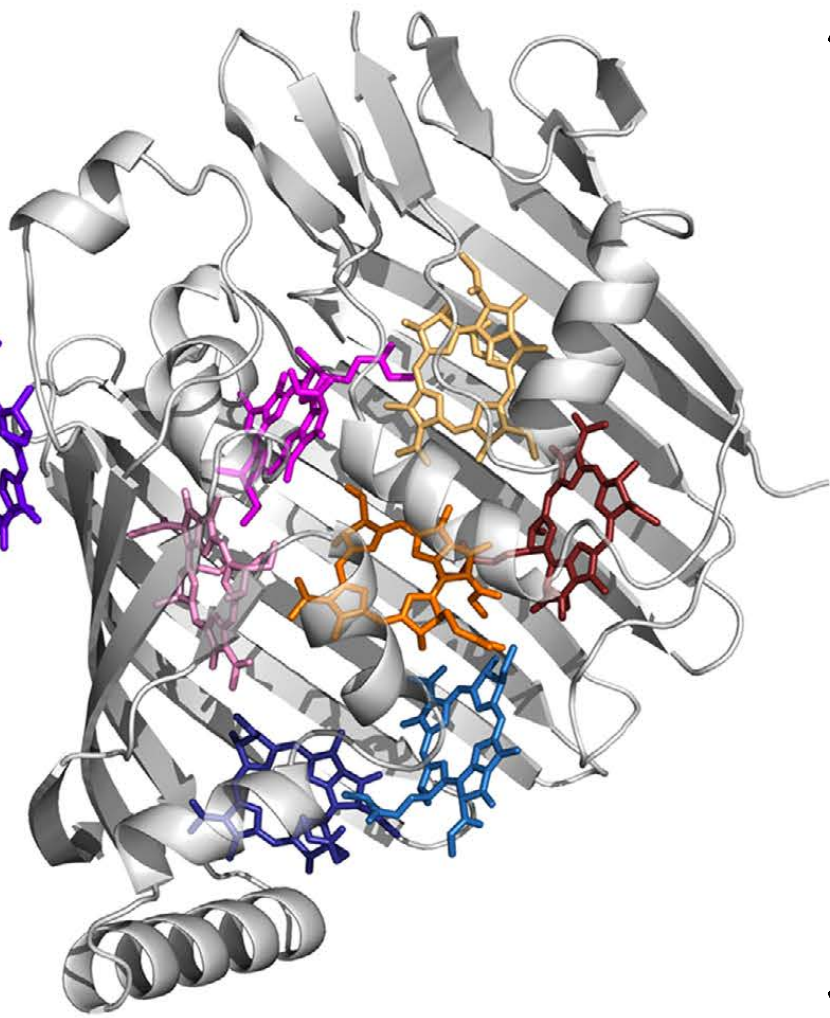


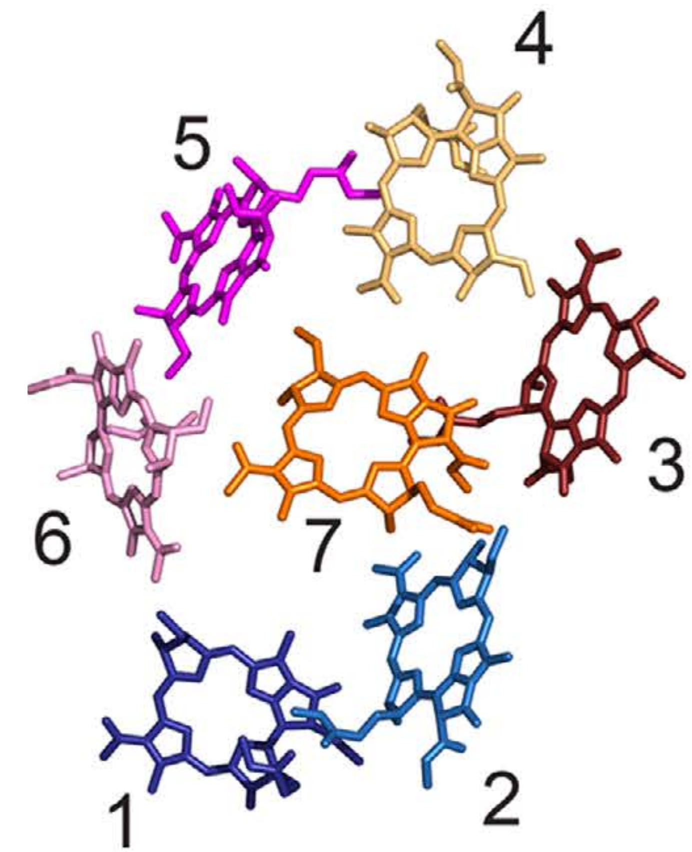
) =



Reduced Density Matrix Formalism

$$\rho(t) = e^{-iHt}\rho(0)e^{iHt}$$

$\mathrm{Tr_B}$ $\Bigg($  $\Bigg)$ =



Reduced Density Matrix Formalism

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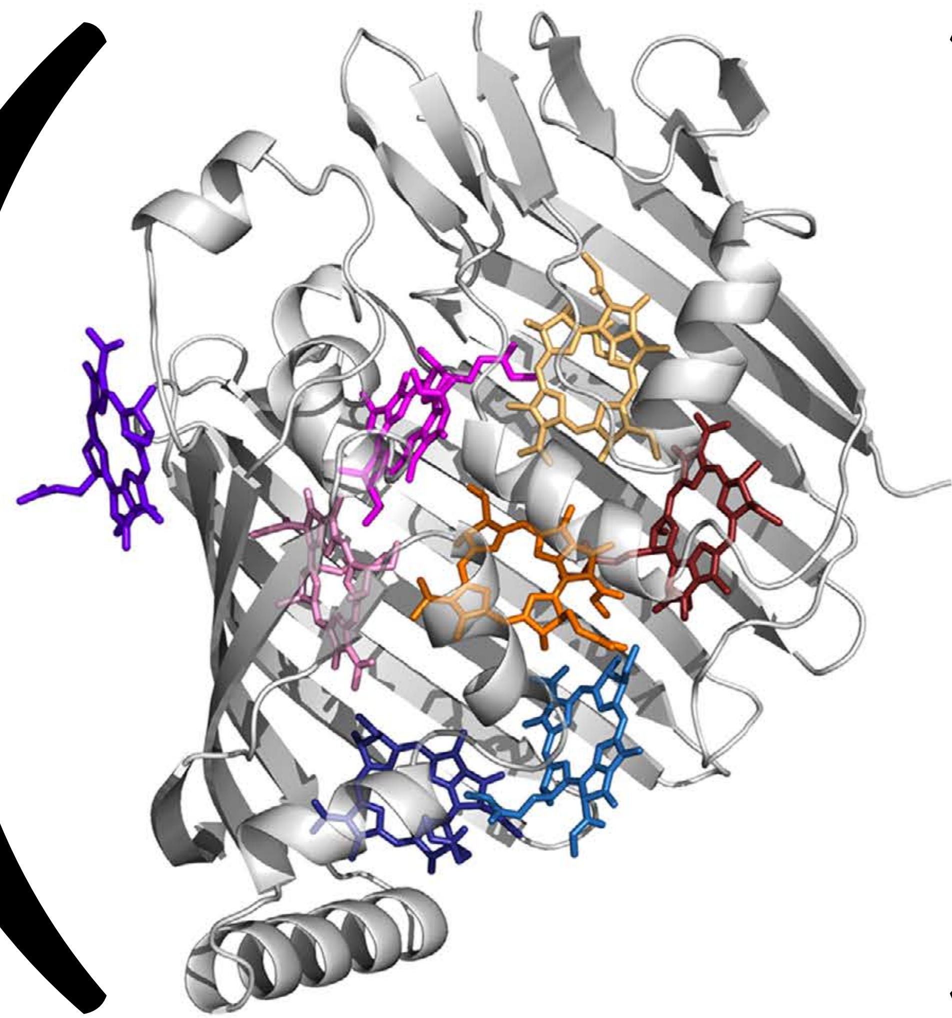
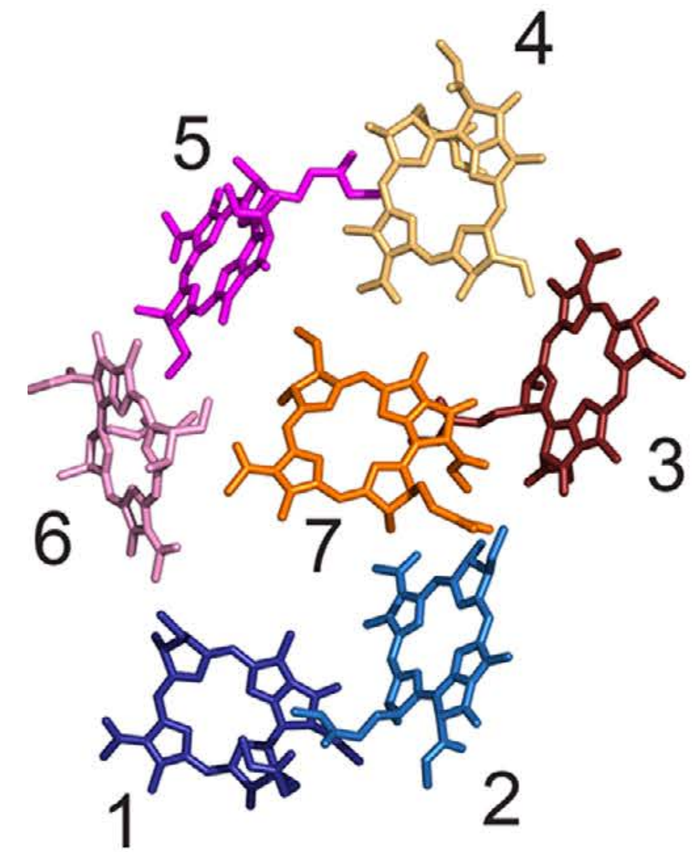
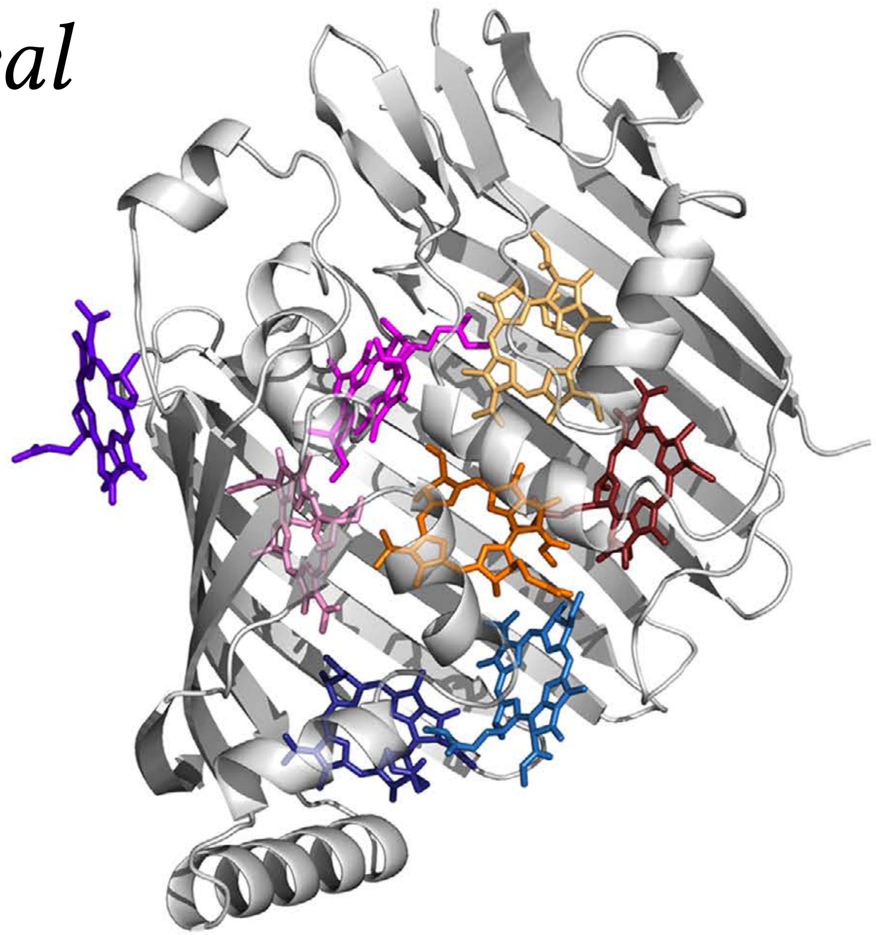
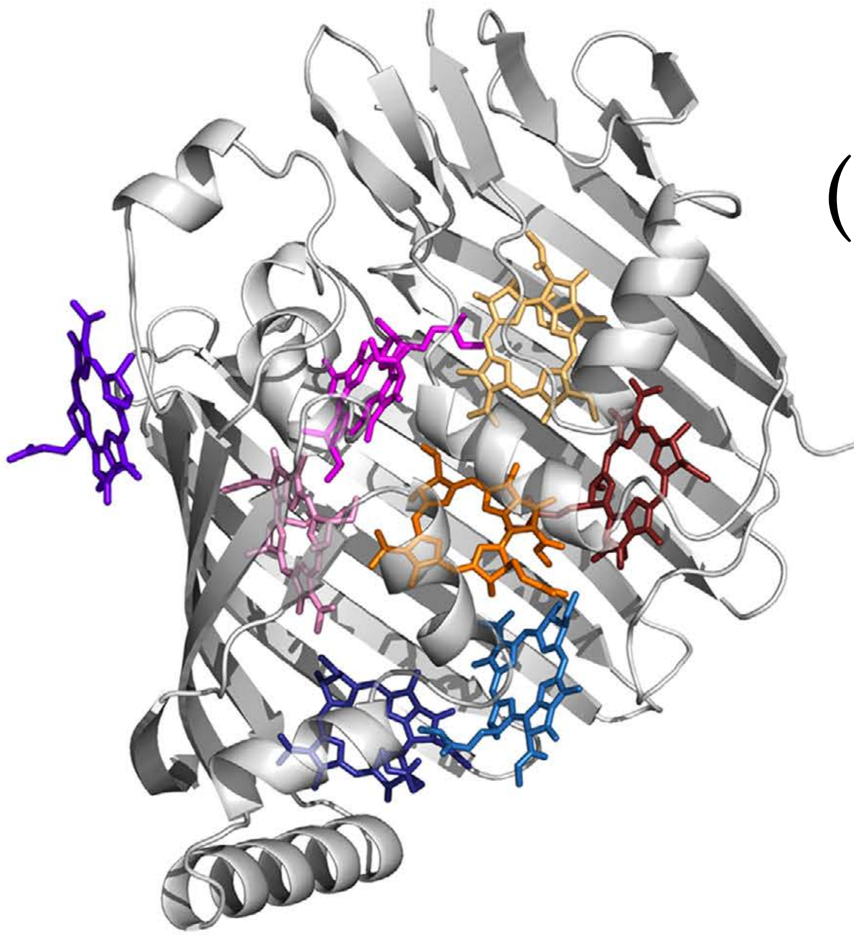
Tr_{B} $\Bigg($  $\Bigg)$ $=$ 

$$\rho_A(t)_I = T_+ \exp\left(-\int_0^t \hat{K}_I^{(2)}(s)ds\right)\rho_A(0)_I$$

Reduced Density Matrix Formalism: NETFD formalism

Physical





Tilde

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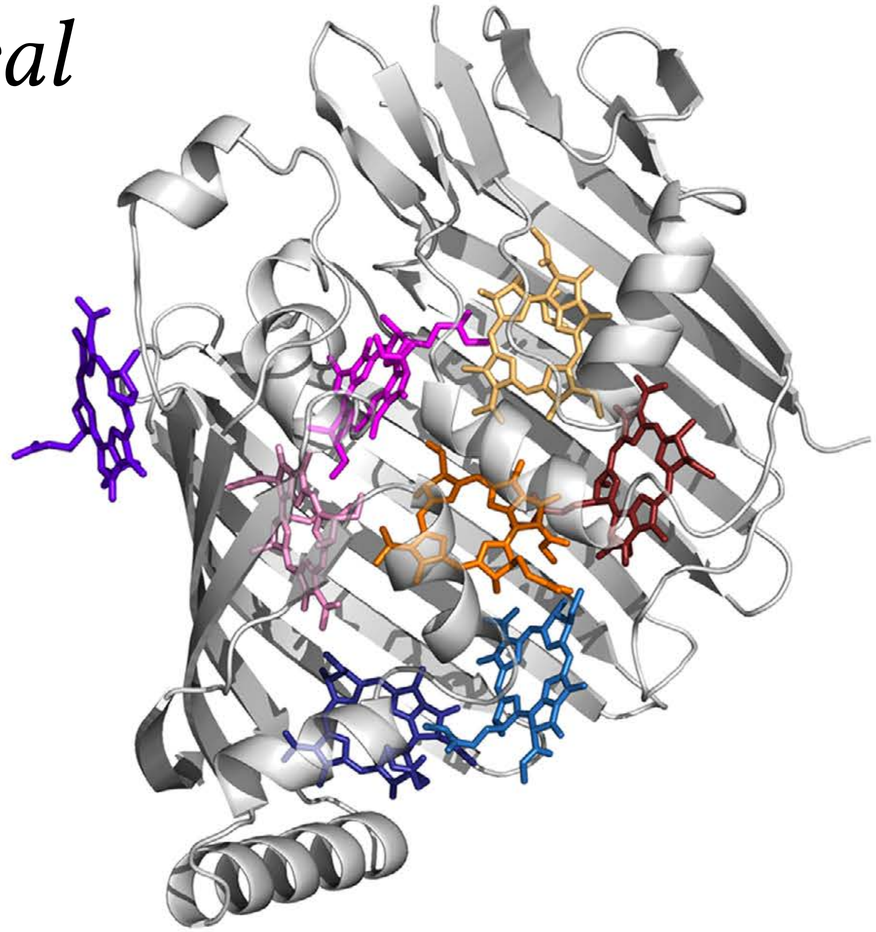
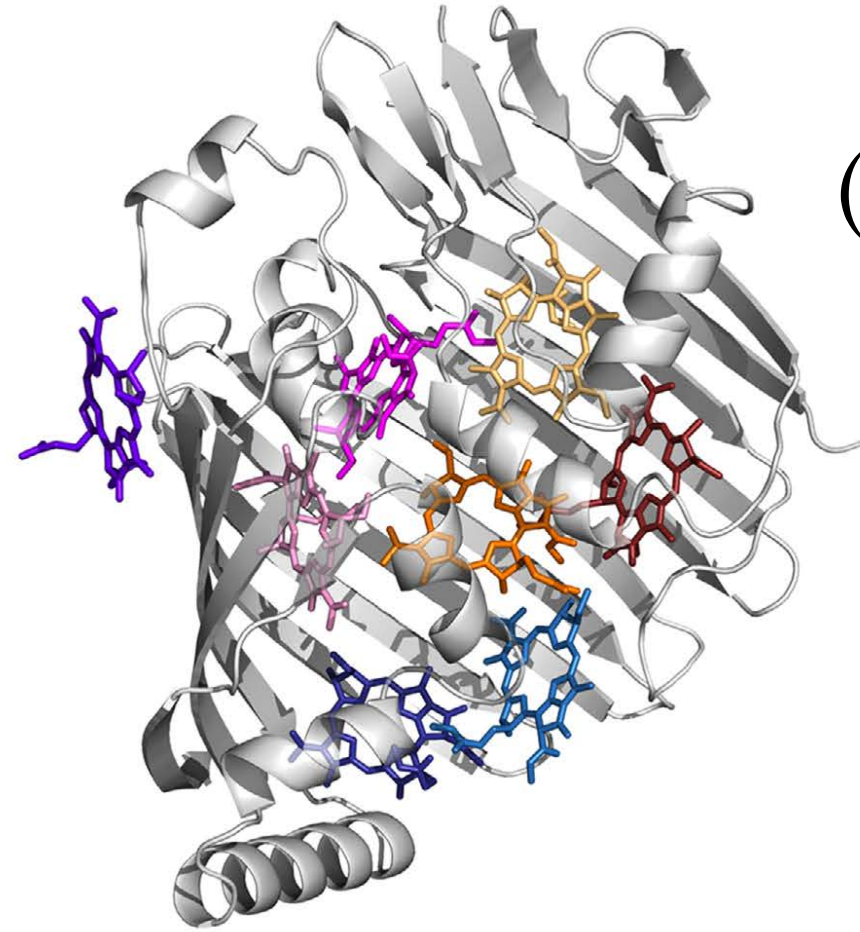
Reduced Density Matrix Formalism: NETFD formalism

Physical





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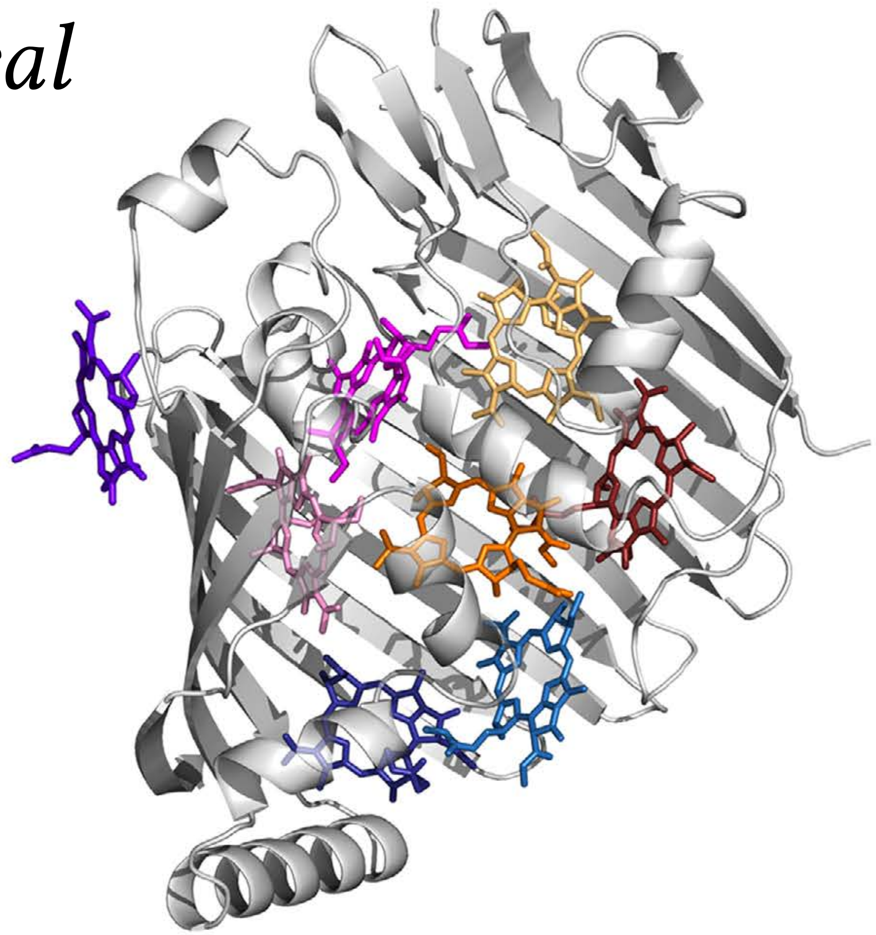
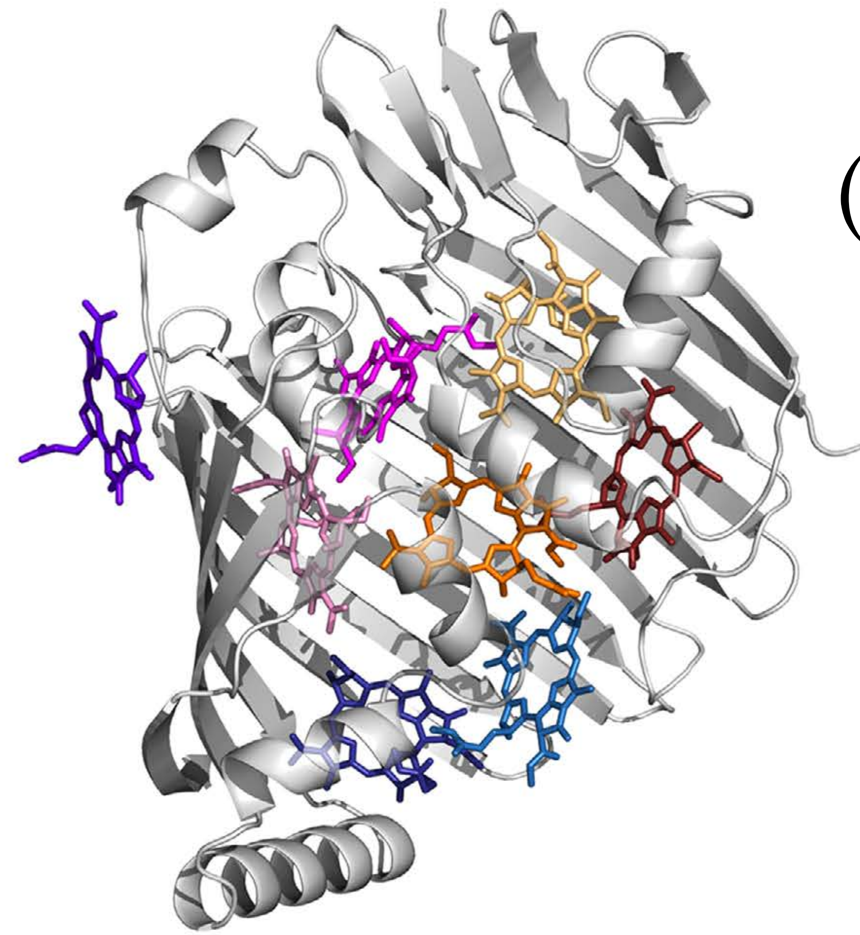
$$\hat{H} = H_A + H_B + V - \tilde{H}_A - \tilde{H}_B - \tilde{V} = \hat{H}_A + \hat{H}_B + \hat{V} = \hat{H}_0 + \hat{V}$$

Reduced Density Matrix Formalism: NETFD formalism

Physical





Tilde

(copy)

$$\hat{H} = H_A + H_B + V - \tilde{H}_A - \tilde{H}_B - \tilde{V} = \hat{H}_A + \hat{H}_B + \hat{V} = \hat{H}_0 + \hat{V}$$

$$|\rho_A(t)\rangle = \sum_{n \in B} \langle n\tilde{n} | \rho(t)\rangle = \langle I_B | \rho(t)\rangle$$

Hierarchical Equation of Motion: NETFD formalism

$$\frac{\partial}{\partial t}|\rho_A^{\mathbf{m}}\rangle = -\left[i(H_A - \tilde{H}_A) + \sum_{kj} m_{kj}\gamma_{kj}\right]|\rho_A^{\mathbf{m}}\rangle$$

$$-i\sum_{kj}\sqrt{m_{kj}/|c_{kj}|}\,(c_{kj}S_k - c_{kj}^{*}\tilde{S}_k)\,|\rho_A^{\mathbf{m}-1_{kj}}\rangle$$

$$-i\sum_{kj}\sqrt{(m_{kj}+1)|c_{kj}|}\,(S_k - \tilde{S}_k)\,|\rho_A^{\mathbf{m}+1_{kj}}\rangle$$

Hierarchical Equation of Motion: NETFD formalism

$$\frac{\partial}{\partial t}\boxed{|\rho_A^{\mathbf{m}}\rangle} = -\left[i(H_A - \tilde{H}_A) + \sum_{kj} m_{kj}\gamma_{kj}\right]|\rho_A^{\mathbf{m}}\rangle$$

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Auxiliary density vector

$|\rho_A\rangle = |\rho_A^0\rangle$

Hierarchical Equation of Motion: NETFD formalism

$$\frac{\partial}{\partial t}\boxed{|\rho_A^{\mathbf{m}}\rangle} = -\left[i(H_A - \tilde{H}_A) + \sum_{kj} m_{kj}\gamma_{kj}\right]|\rho_A^{\mathbf{m}}\rangle \qquad C_k(t) = \sum_j c_{kj} e^{-\gamma_{kj}t}$$

$$-i\sum_{kj}\sqrt{m_{kj}/|c_{kj}|}\,(c_{kj}S_k - c_{kj}^{*}\tilde{S}_k)\,|\rho_A^{\mathbf{m}-1_{kj}}\rangle$$

$$-i\sum_{kj}\sqrt{(m_{kj}+1)|c_{kj}|}\,(S_k - \tilde{S}_k)\,|\rho_A^{\mathbf{m}+1_{kj}}\rangle$$

Auxiliary density vector

$$|\rho_A\rangle = |\rho_A^{0}\rangle$$

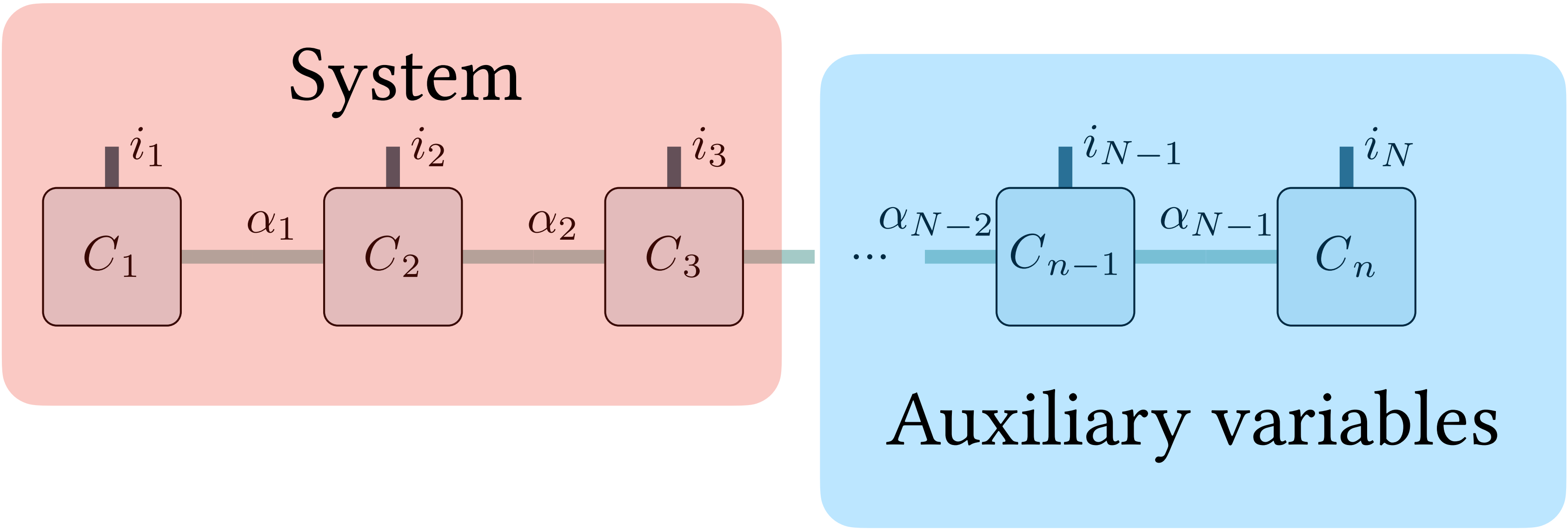
TT implementation of HEOM

$$|\rho(t)\rangle = \sum_{i_1,i_2,\ldots,i_N} C(i_1,\ldots,i_N;t)\,|i_1\rangle \otimes |i_2\rangle \cdots |i_N\rangle$$

TT implementation of HEOM

$$|\rho(t)\rangle = \sum_{i_1,i_2,\ldots,i_N} C(i_1,\ldots,i_N;t)\,|i_1\rangle \otimes |i_2\rangle \cdots |i_N\rangle$$

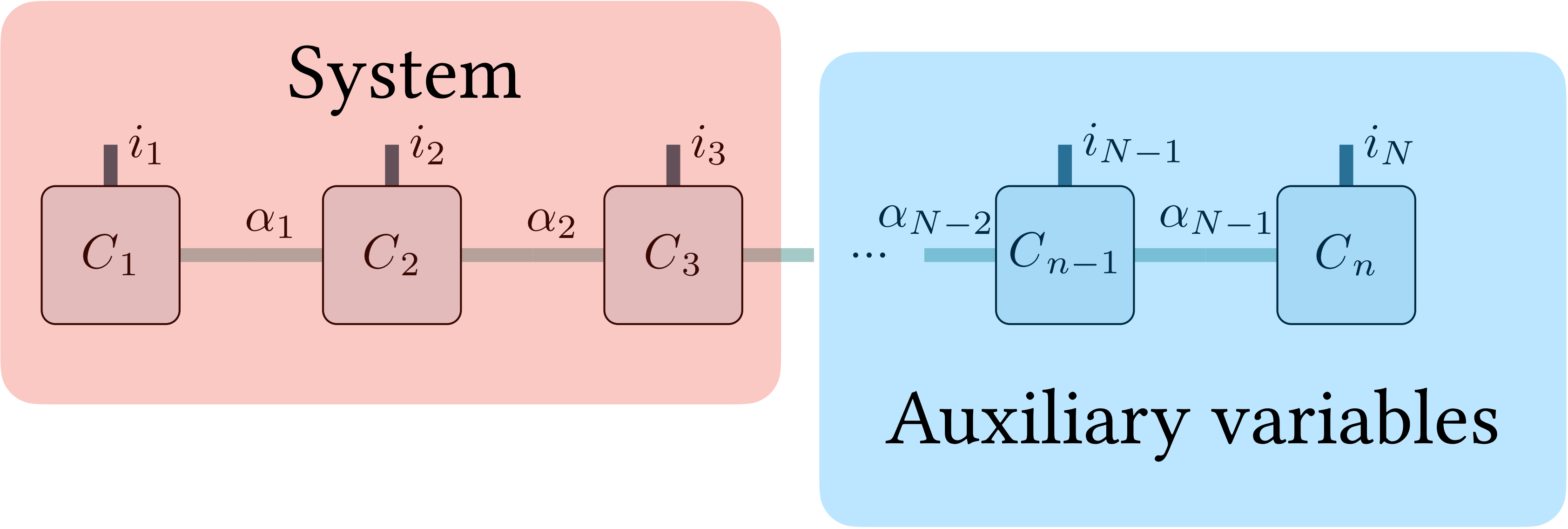
$$|\rho(t)\rangle =$$



TT implementation of HEOM

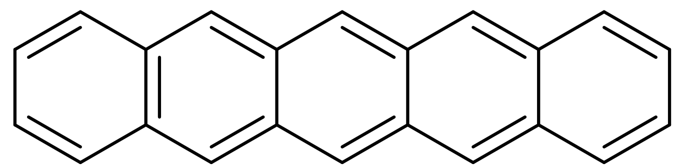
$$|\rho(t)\rangle = \sum_{i_1,i_2,\ldots,i_N} C(i_1,\ldots,i_N;t)\,|i_1\rangle \otimes |i_2\rangle \cdots |i_N\rangle$$

$|\rho(t)\rangle =$

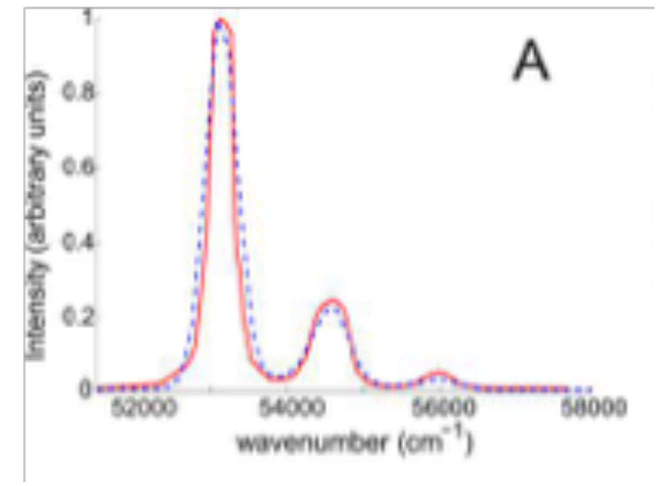


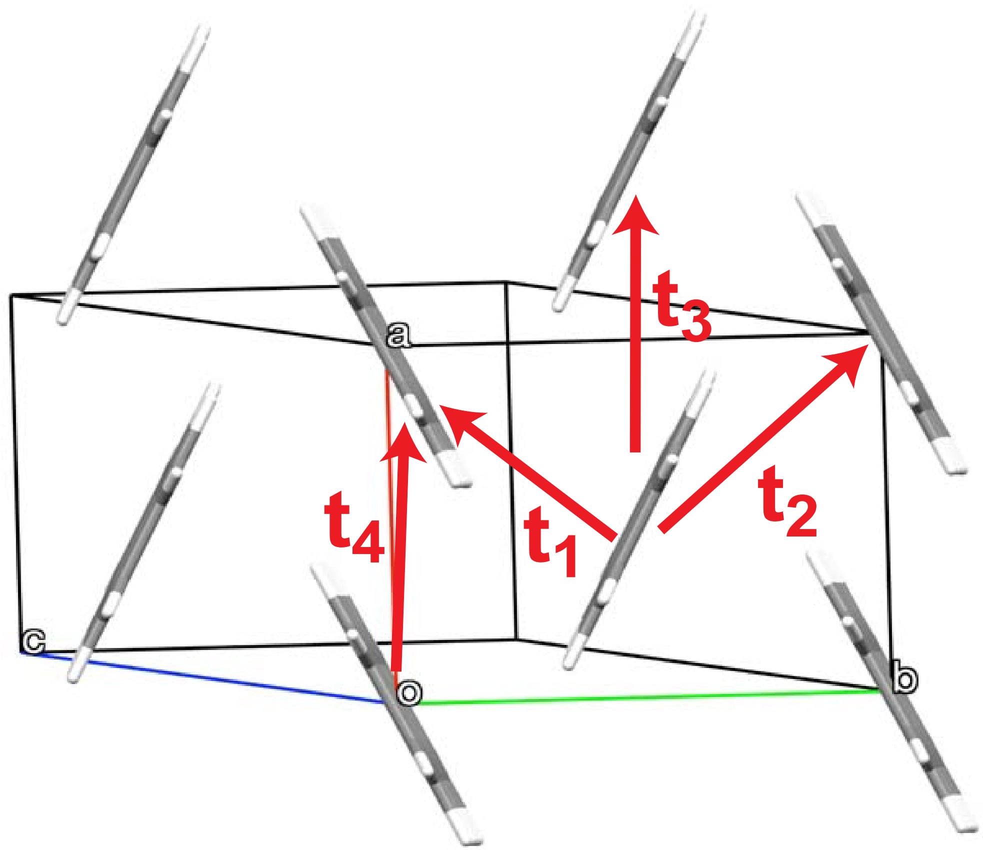
$$\frac{d}{dt}\big|\rho(C(t))\big\rangle = -i\hat{P}_{\mathcal{T}(C(t))}X\big|\rho(C(t))\big\rangle$$

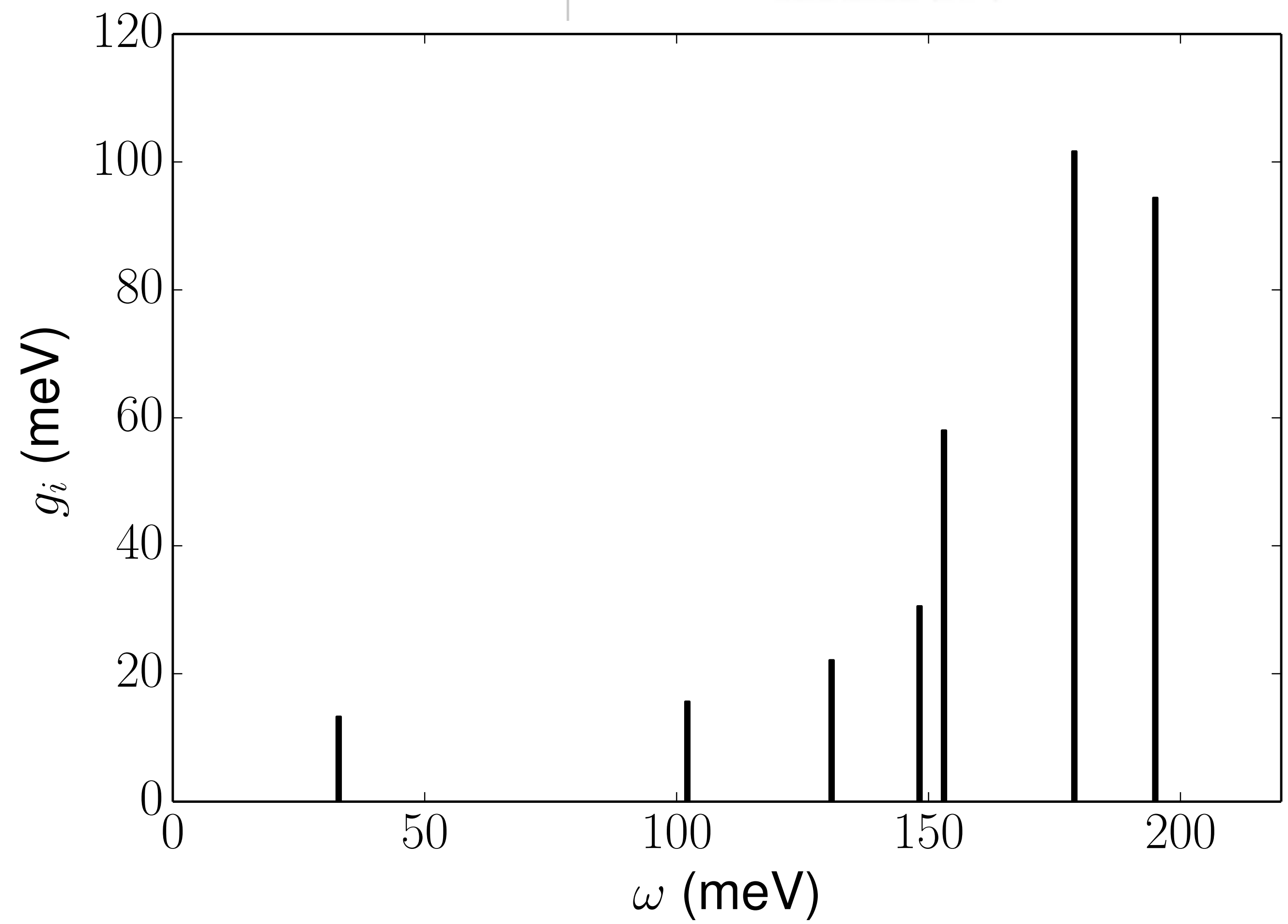
Charge-transport in molecular crystals



Pentacene







t_1 = 75 meV
t_2 = 32 meV
t_3 = 20 meV
t_4 = 6 meV

Brédas, Nat. Comm. 2015
Brédas, JACS, 2010

Linear vibronic couplings of P/P$^+$ couple.
Reorganization energy E_r = 577 cm^{-1}

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Charge-transfer in a pentacene dimer in condensed phase

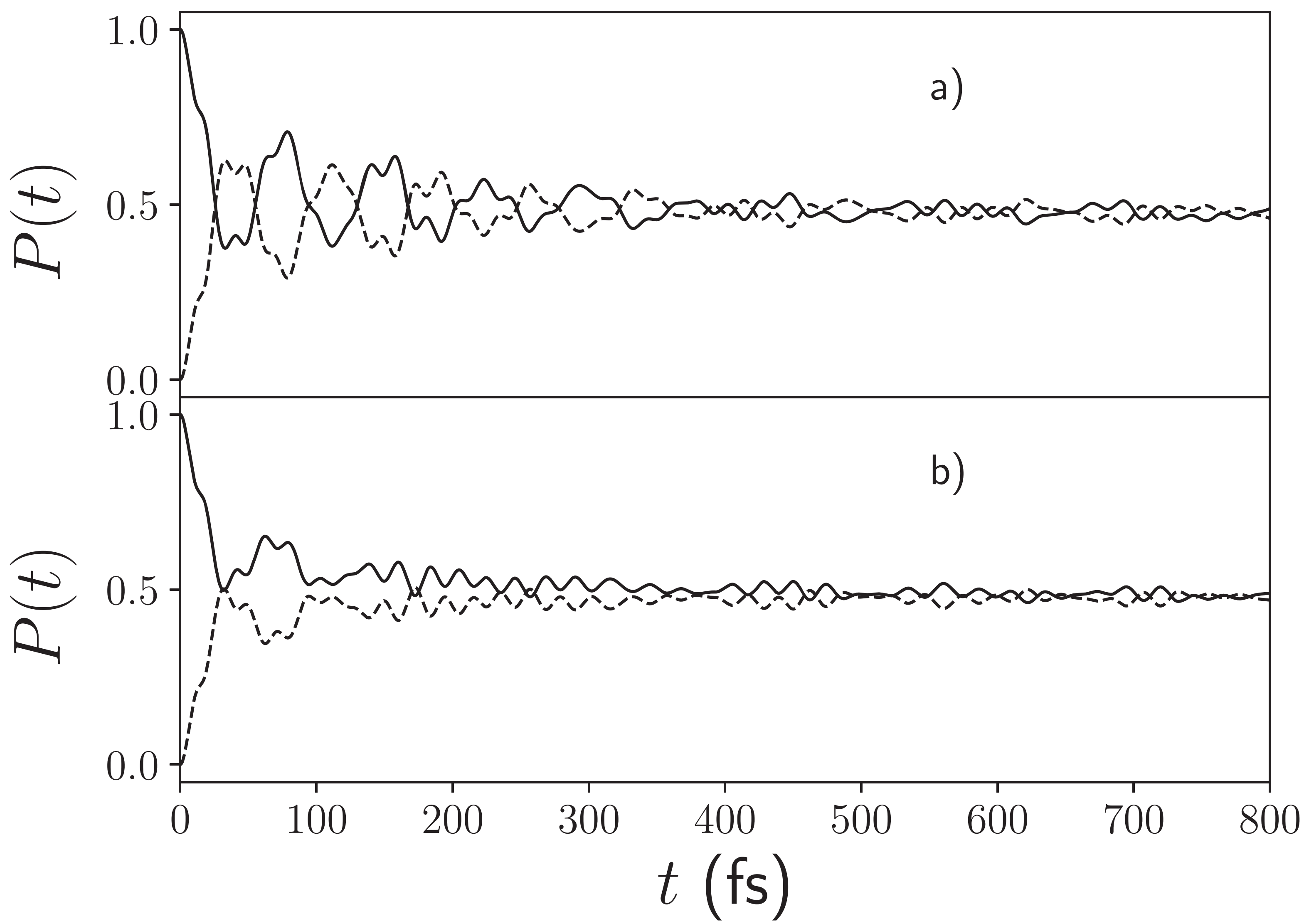


FIG. 4. Population dynamics of a homodimer with 14 nuclear vibrations. Bath reorganization energies are (a) λ = 90 cm^{-1} and (b) λ = 300 cm^{-1}. Converged results are obtained with TT rank 115. The hierarchy level is truncated at m = 10 on each bath.

Charge-transfer in a pentacene dimer in condensed phase: effect of TT *rank* / MPS *bond dimension*

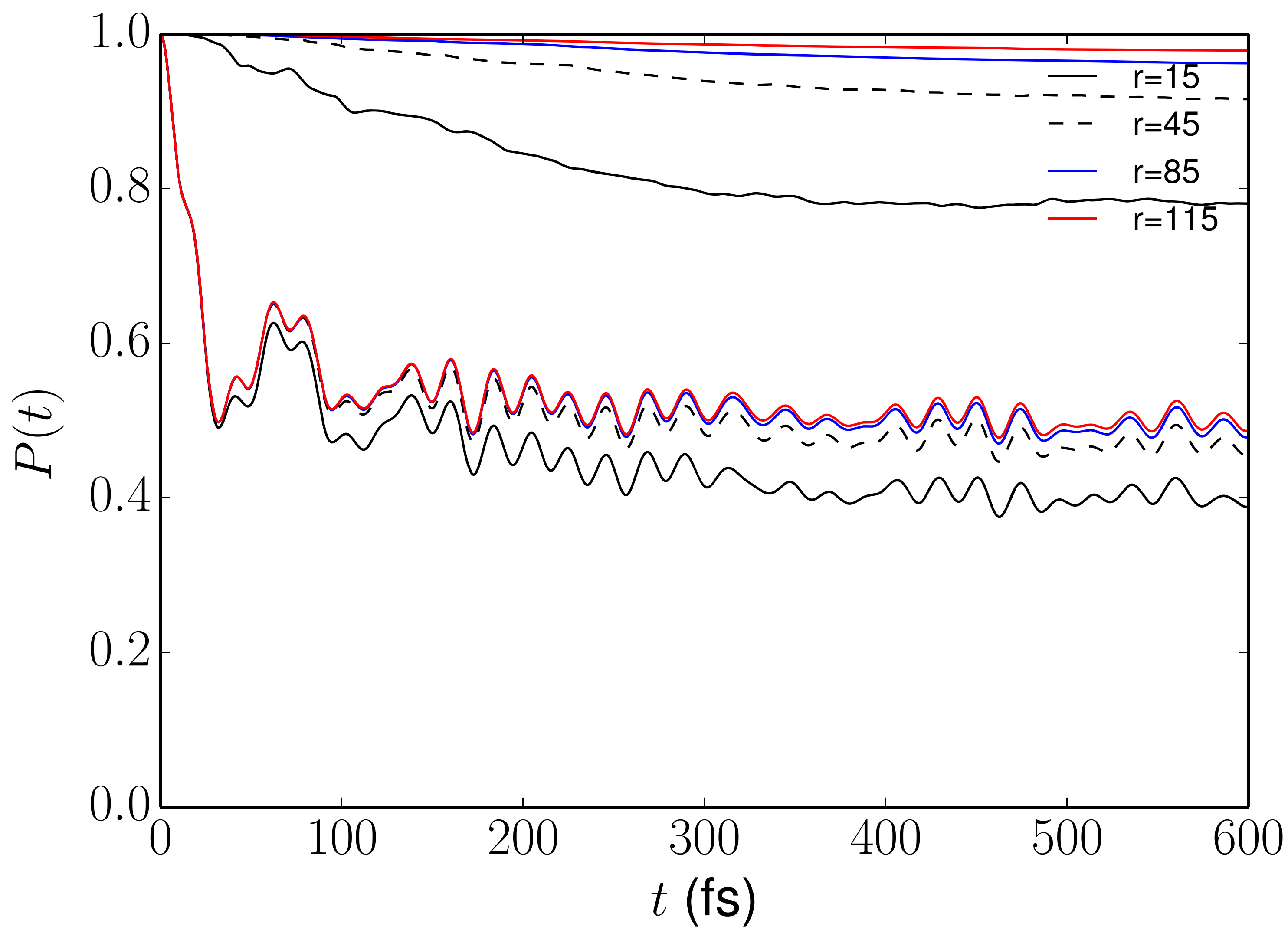
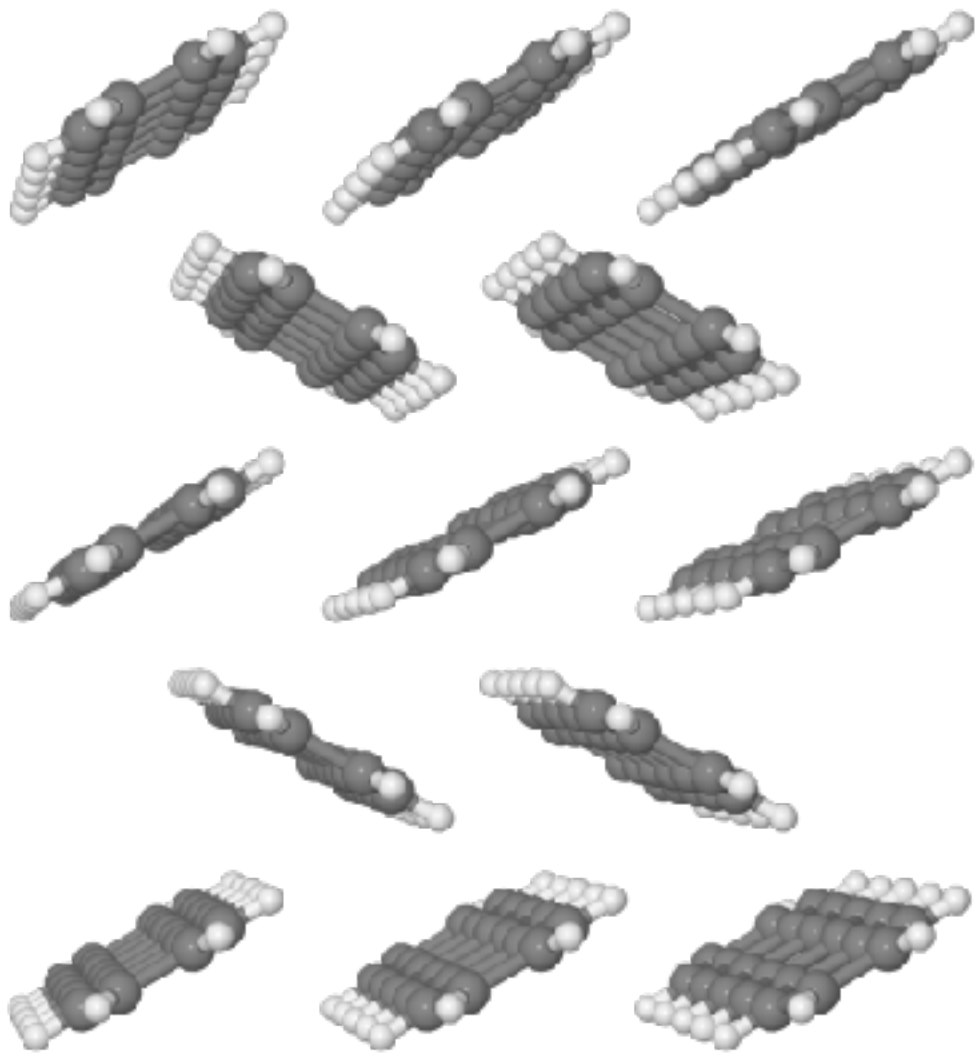
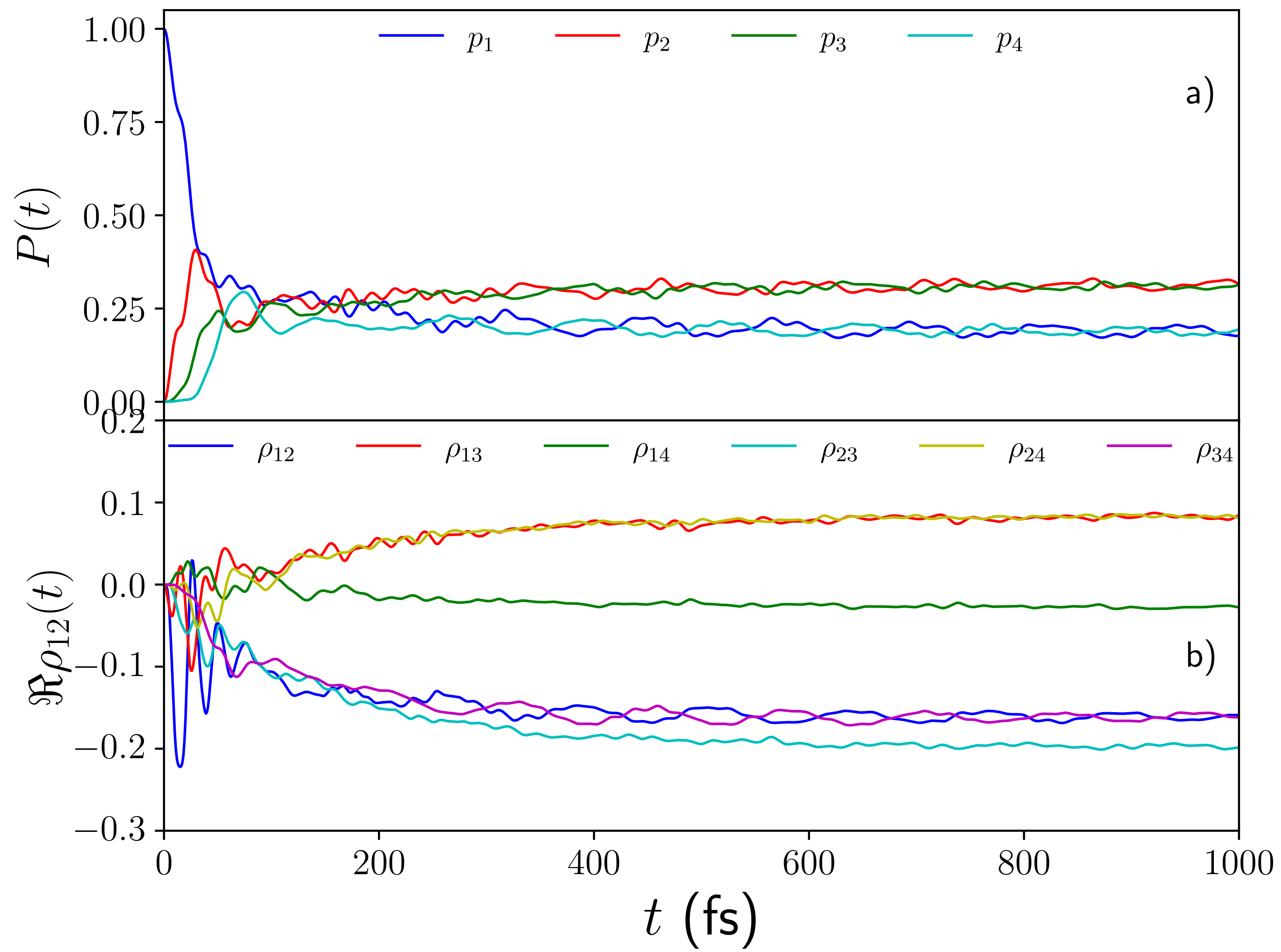


FIG. 5. Population dynamics of the initial electronic state of the homodimer model and overall norm of the state vector for different TT truncation ranks as indicated in the legend. The hierarchy level is truncated at m = 10 on each bath.

Charge-transfer in a pentacene tetramer in condensed phase





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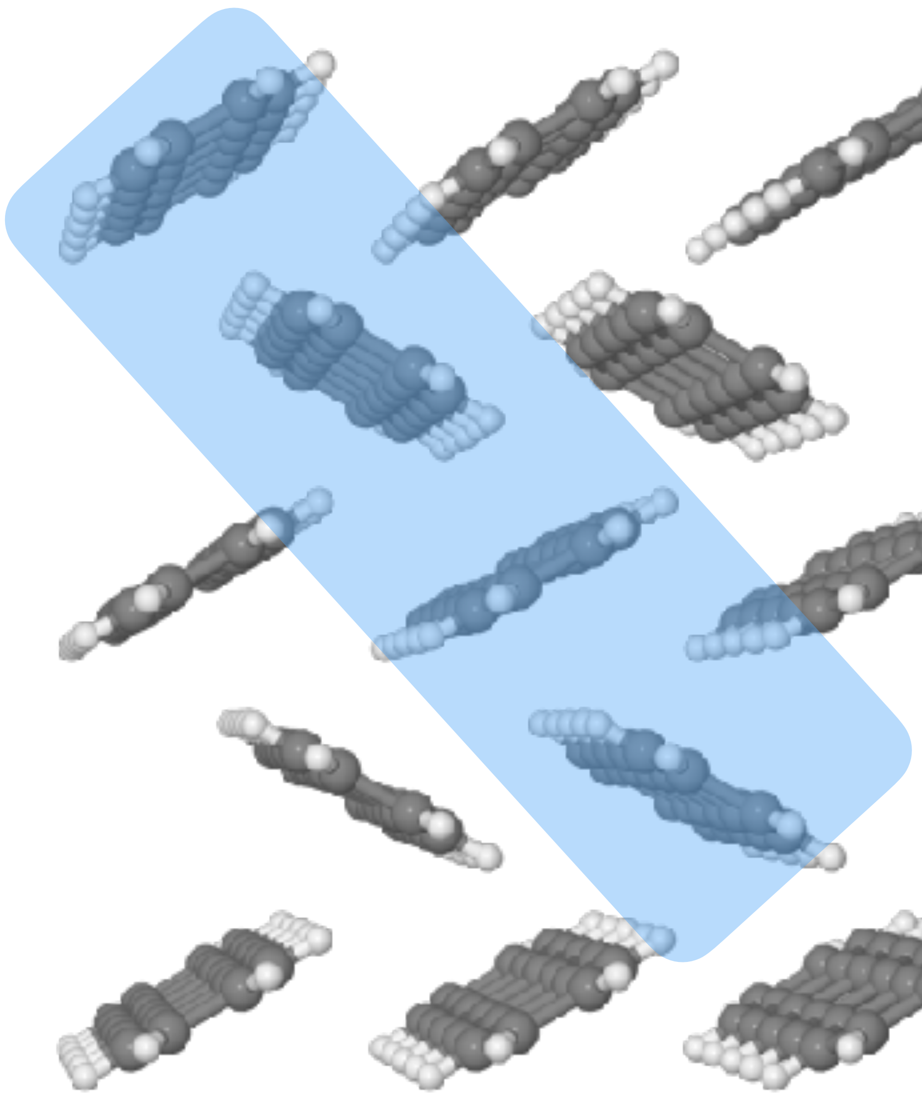
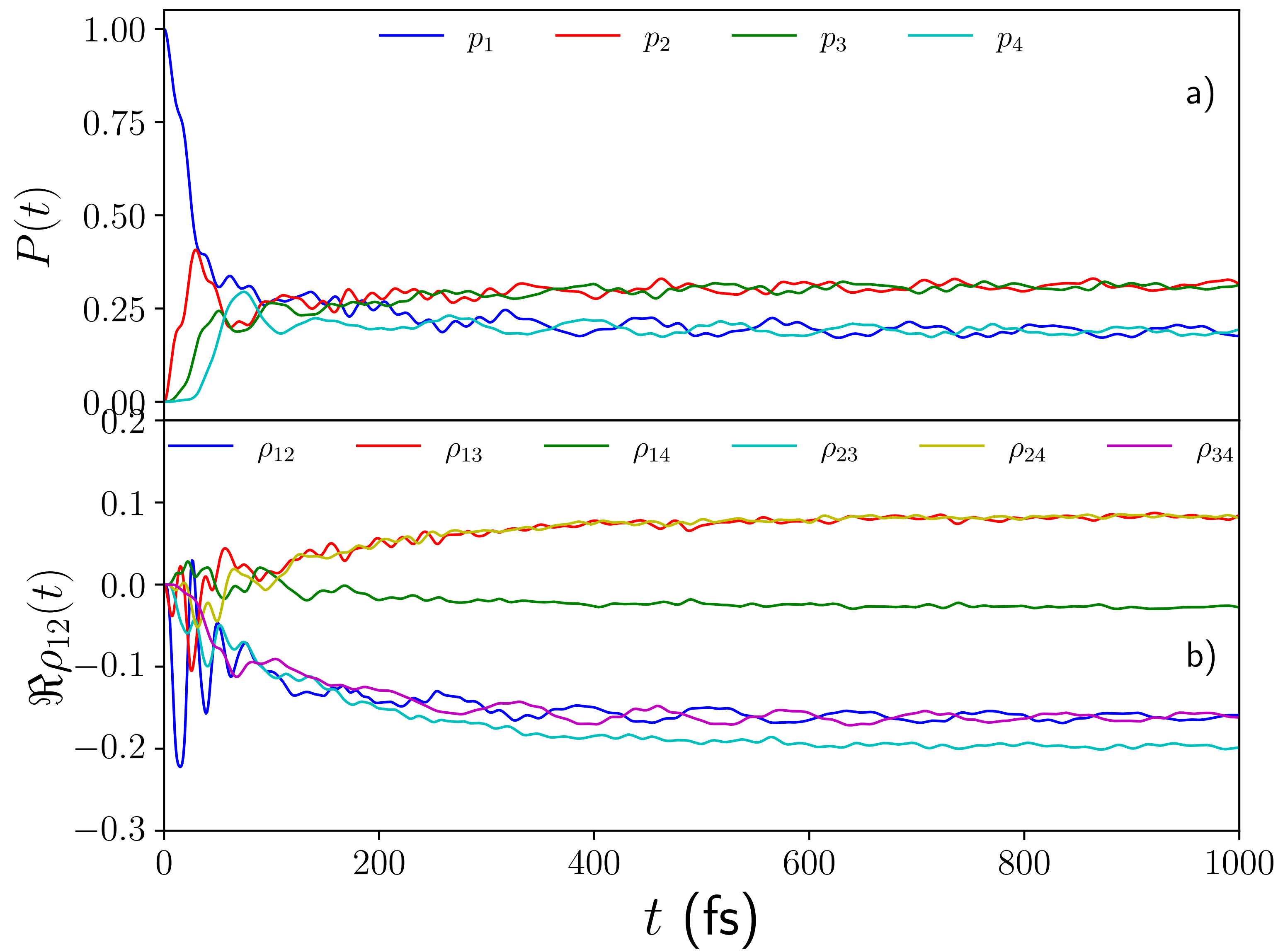
Charge-transfer in a pentacene tetramer in condensed phase





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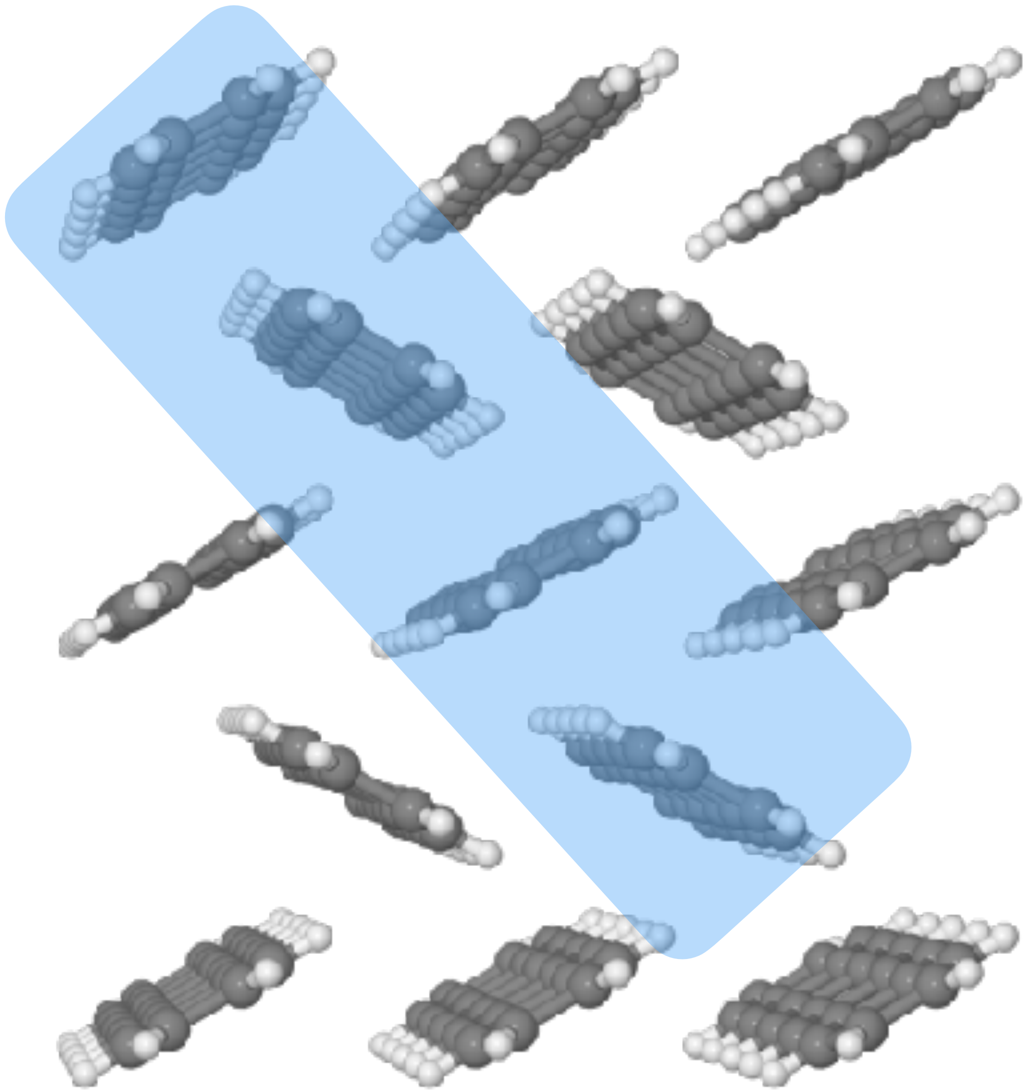
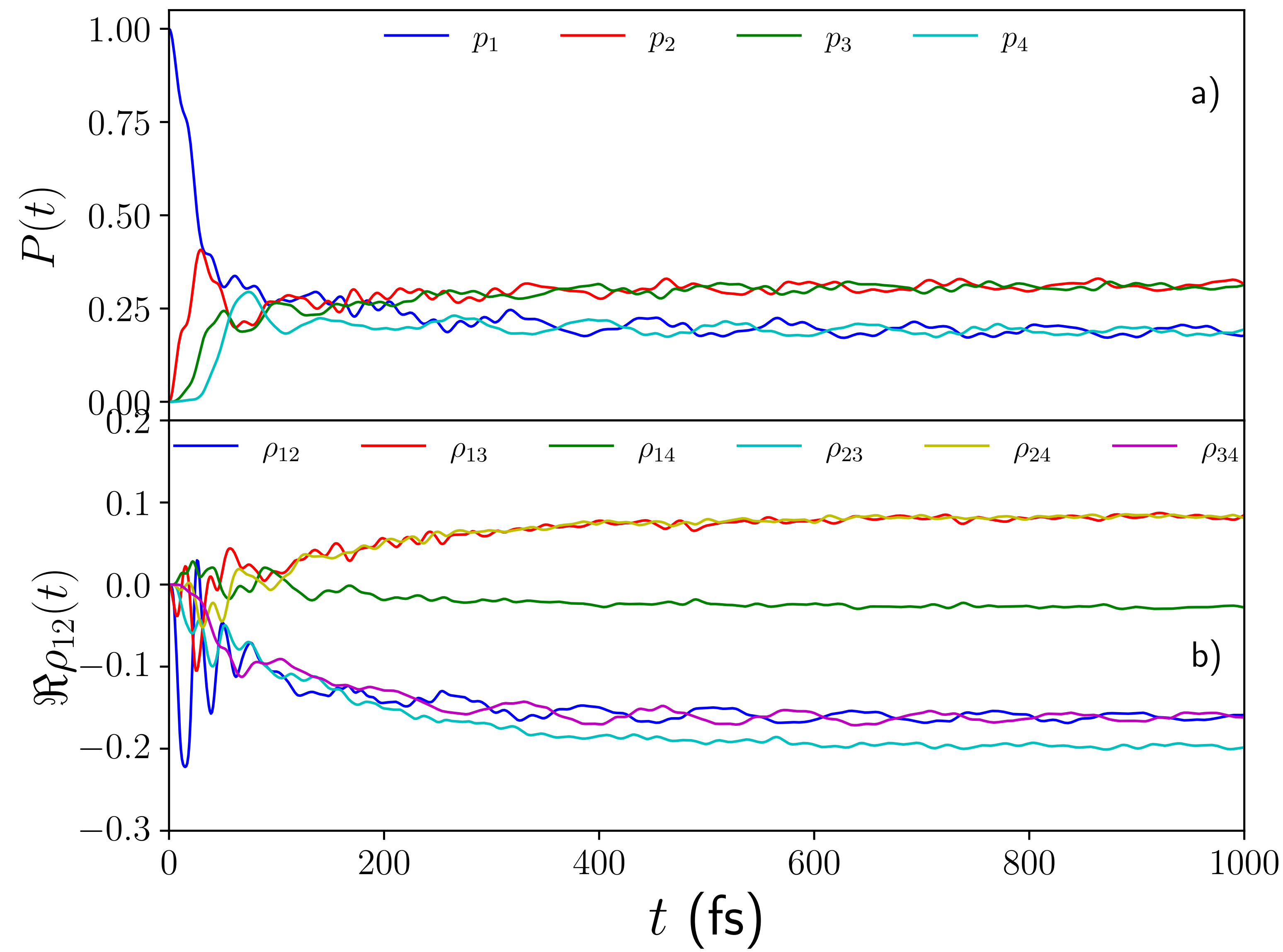
Charge-transfer in a pentacene tetramer in condensed phase

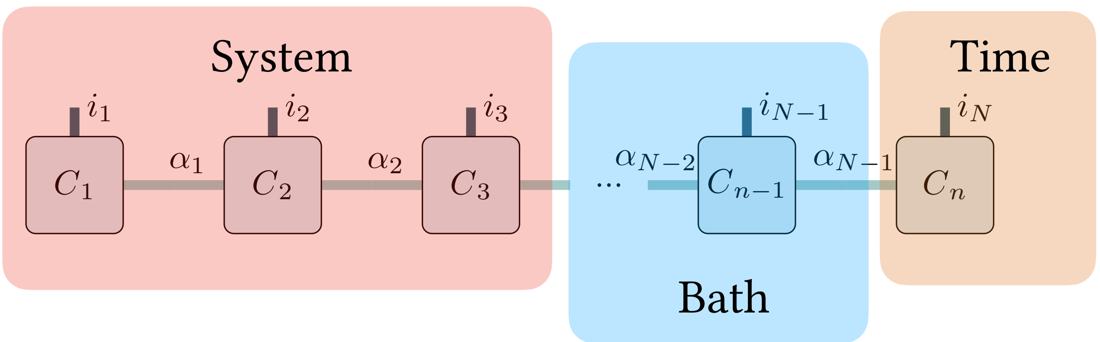




tAMEn algorithm

(Dolgov 2018)

$|\rho(t)\rangle =$



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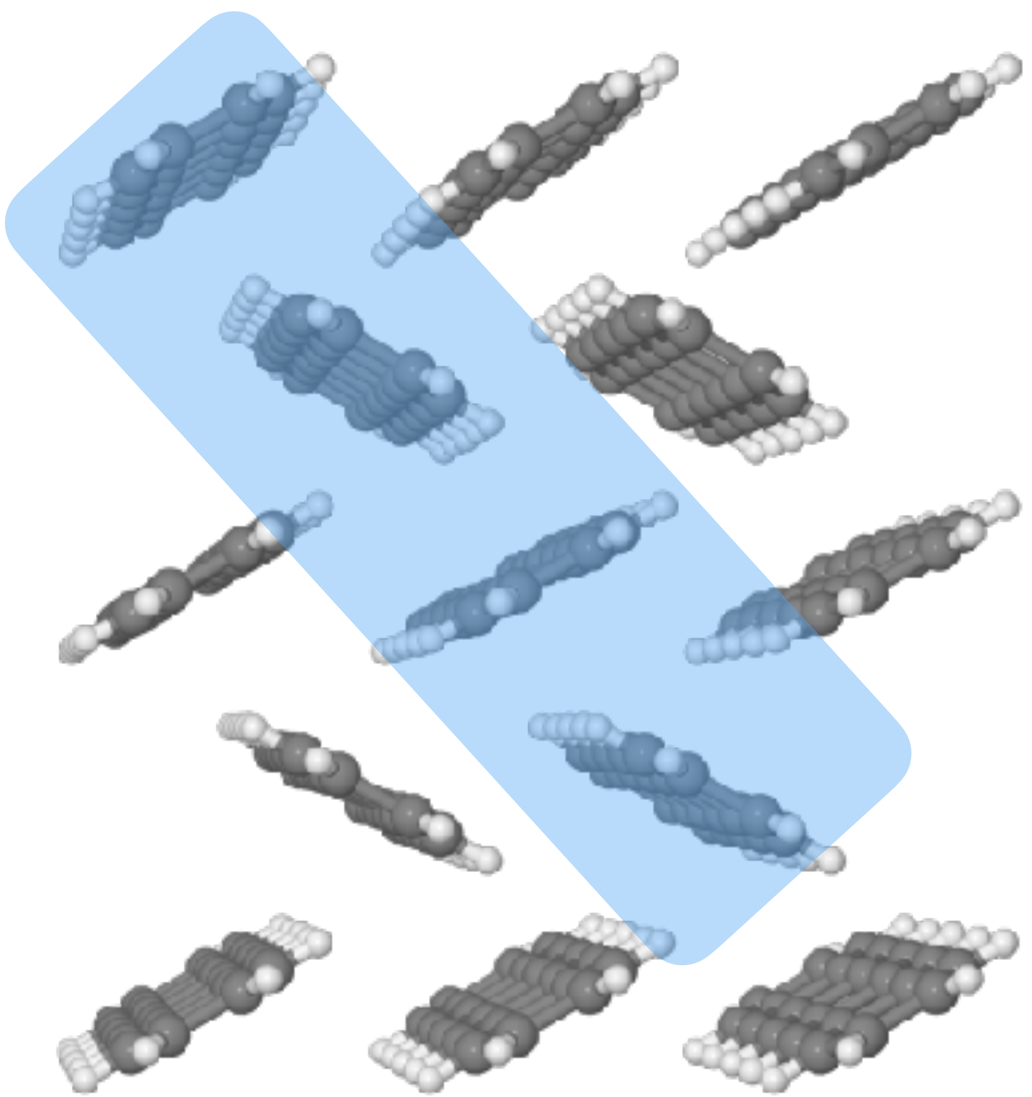
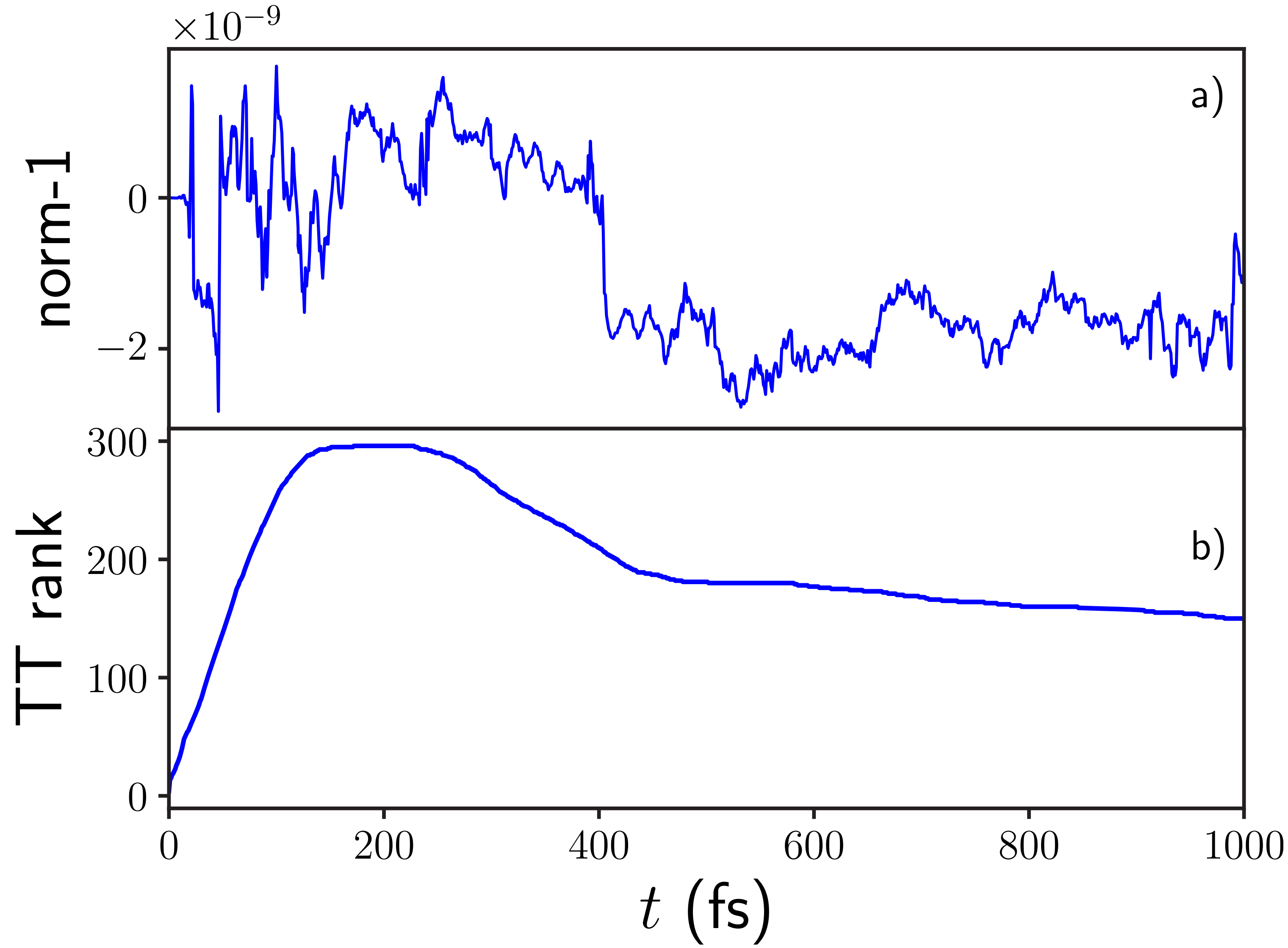
Charge-transfer in a pentacene tetramer in condensed phase

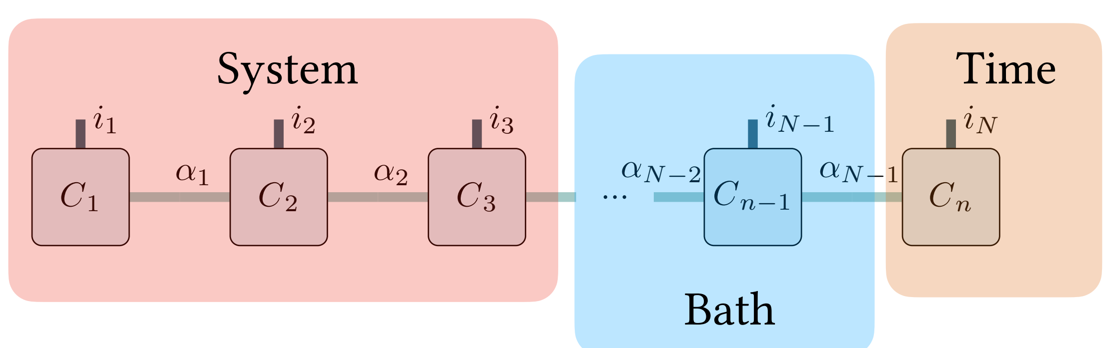




tAMEn algorithm

(Dolgov 2018)

$$|\rho(t)\rangle =$$



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- HEOM formulation in NETFD formalism is very effective for TT implementation
- TT/MPS can handle very large electron-vibrational dynamical problem
- The methodology can be applied to electron baths, and anharmonic systems

Acknowledgements

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Thank you!