VISTA
Virtual International Seminar on
Theoretical Advancements (VISTA)

清華大學 化学系
Department of chemistry, Tsinghua University

Time-Dependent Density Matrix Renormalization Group for Electron-Vibration Coupled Problems

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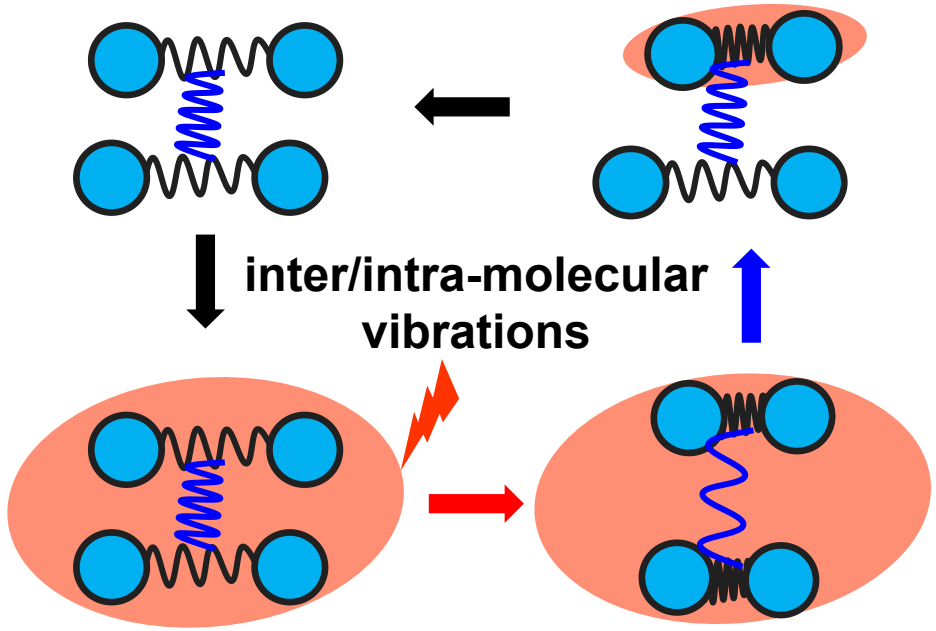
10/14/2021

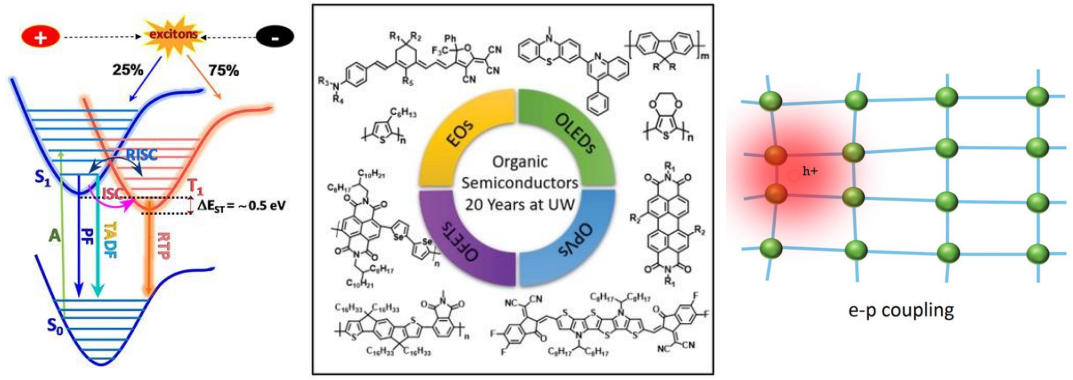
Electron-vibration coupled problems

Organic molecules are flexible

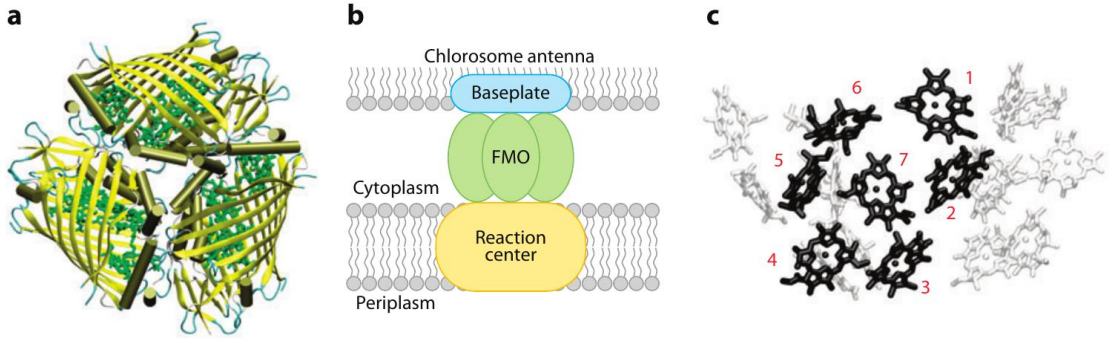
electron motion ⇌ nuclear motion



Decoherence and dissipation of electronic states



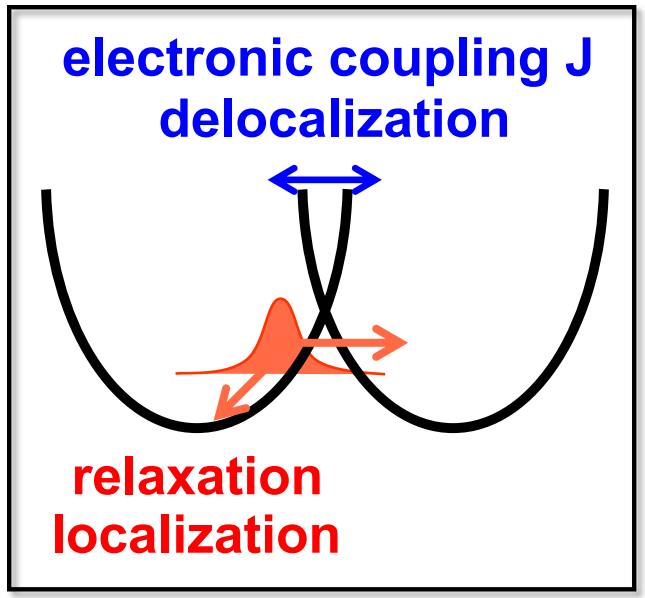
Luscombe, C. K. *et al.* *Adv. Mater.* 2021, 33, 1904239.

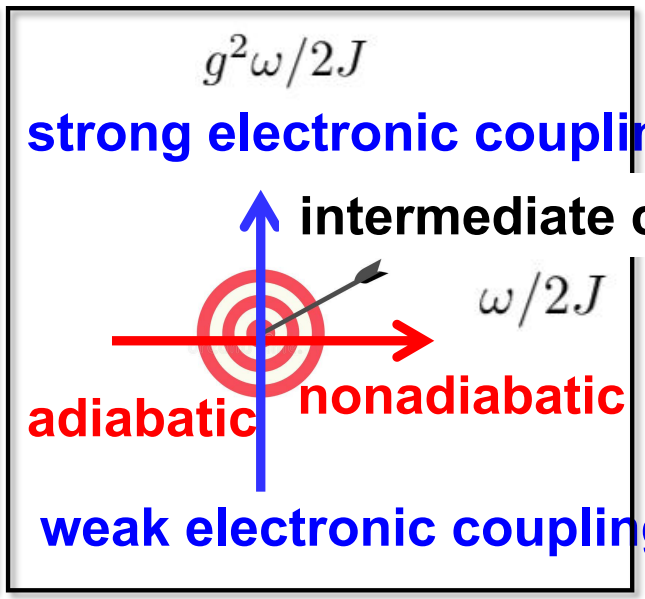


Fleming, G. R. *et al.* *Annu. Rev. Phys. Chem.* 2009, 60, 241.

Electron-vibration coupling is key to light-emitting, charge/energy transfer/transport in organic optoelectronic materials and biological systems

Theoretical challenges





$$|\Psi\rangle = \sum_{\{\sigma\}} C_{\sigma_1\sigma_2\cdots\sigma_N} |\sigma_1\sigma_2\cdots\sigma_N\rangle$$

N	Memory
5	1.6 M
10	160 G
50	10^{41} G
scaling	~ O(10^N)

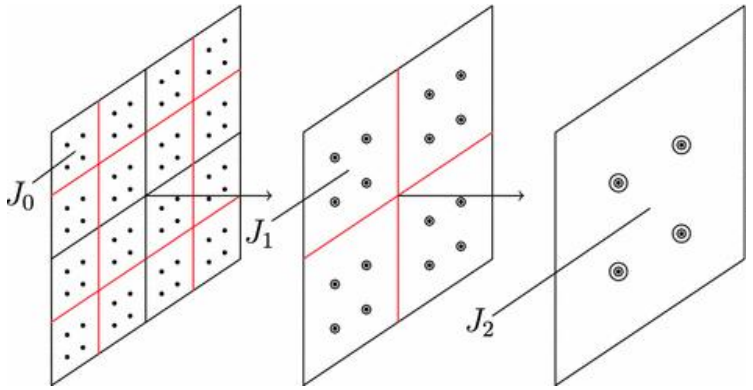
10 basis for 1 DoF

1. approximate method is not universally applicable
2. quantum exponential wall for many-body wavefunction theory

Density matrix renormalization group

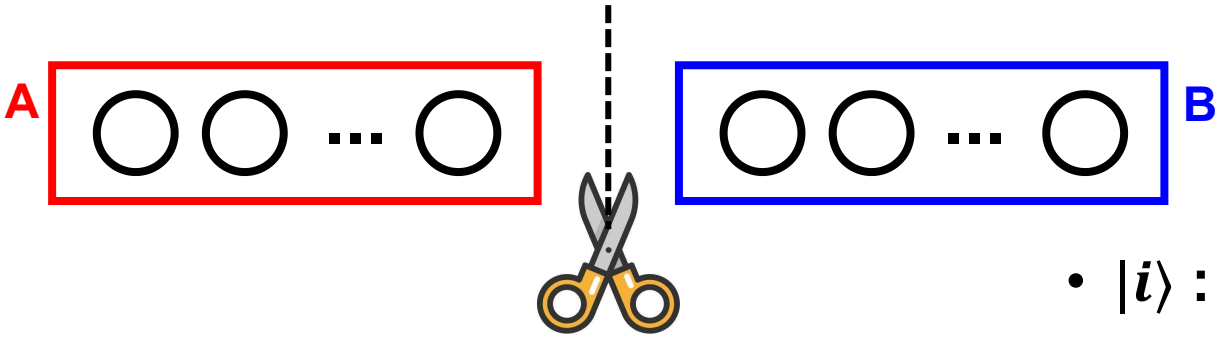
The idea of RG:

effective DoFs (states) with effective interaction



Images from Steinwachs, C. F.
Springer International Publishing 2014.

DMRG: truncation scheme based on reduced density matrix



A subspace + B subspace

$$\rho_A = \mathrm{Tr}_B(\rho) = \mathrm{Tr}_B(|\Psi\rangle\langle\Psi|) = \sum_i^{\min(a,b)} w_i |i\rangle_A \langle i|_A$$

$$\sum_i w_i = 1$$

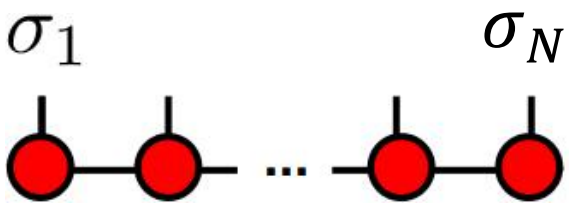
White, S. R. *Phys. Rev. Lett.* 1992, 69, 2863.

- $|i\rangle$: renormalized states
- w_i : weight of renormalized state
- Entanglement: von Neumann entropy

$$S = \sum_i -w_i \log w_i$$

- The first M renormalized states form the best approximation in the 2-norm

Matrix product state (MPS)

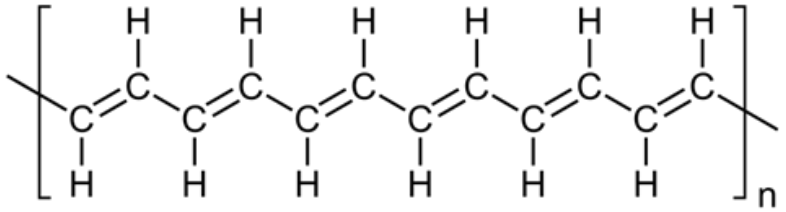


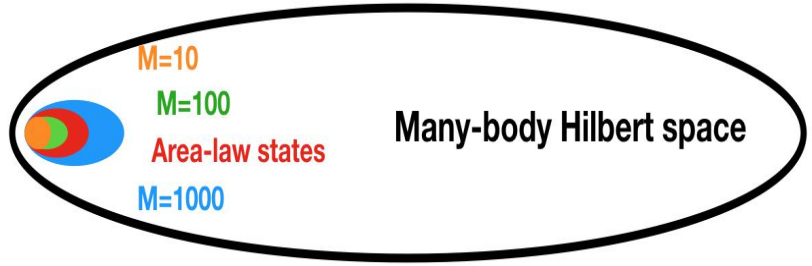
$$|\Psi\rangle = \sum_{\{\sigma\}} C_{\sigma_1\sigma_2\cdots\sigma_N} |\sigma_1\sigma_2\cdots\sigma_N\rangle$$

$$= \sum_{\{a\},\{\sigma\}} A^{\sigma_1}_{a_1} A^{\sigma_2}_{a_1 a_2} \cdots A^{\sigma_N}_{a_{N-1}} |\sigma_1\sigma_2\cdots\sigma_N\rangle$$

The size of a (bond dimension M_S) controls the accuracy

- **Locality in physics**





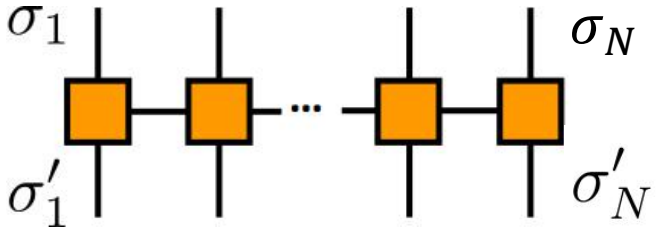
- **Locality in math**

The complexity of algorithm is polynomial

Schollwöck, U. *Ann. Phys.* 2011, 326, 96–192.
Ostlund, S.; Rommer, S. *Phys. Rev. Lett.* 1995, 75, 3537.

Matrix product operator (MPO)

$$\hat{O} = \sum_{\{a\},\{\sigma\},\{\sigma'\}} W_{a_1}^{\sigma_1,\sigma_1'} W_{a_1 a_2}^{\sigma_2,\sigma_2'} \cdots W_{a_{N-1}}^{\sigma_N,\sigma_N'} |\sigma_1\sigma_2\cdots\sigma_N\rangle \langle\sigma_1'\sigma_2'\cdots\sigma_N'|$$



Crosswhite, G. M.; Bacon, D. *Phys. Rev. A* 2008, 78, 012356.

MPO takes advantage of the sparsity in operator, and the bond dimension M_O is much smaller than the number of operator terms.

e.g. $$\hat{H}_{\text{Holstein}} = \sum_i \varepsilon_i a_i^\dagger a_j + \sum_{i\neq j} J_{ij} a_i^\dagger a_j + + \sum_{in} \frac{1}{2}(p_{in}^2 + \omega_{in}^2 x_{in}^2) + \sum_{in} c_{in} a_i^\dagger a_i x_{in}$$

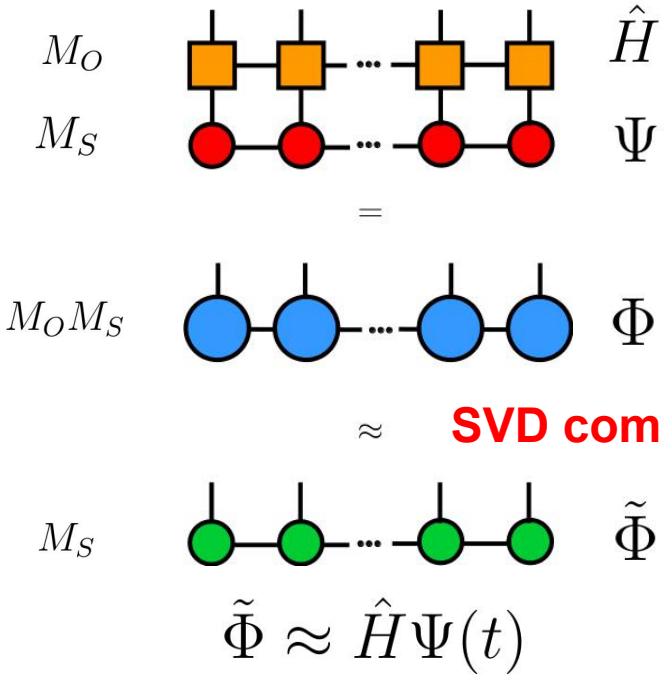
The number of terms is $O(N_{mol}\, N_{vib})$, the full matrix representation is of size $O(2^{N_{mol}}\, d^{N_{mol}N_{vib}})$.

If written in MPO, $M_O = 5$ for 1D nearest neighbor hopping, otherwise $O(N_{mol})$.

TD-DMRG

Propagation and Compression (P&C)

$$\Psi(t+dt) = \Psi(t) - i\hat{H}\Psi(t)dt$$

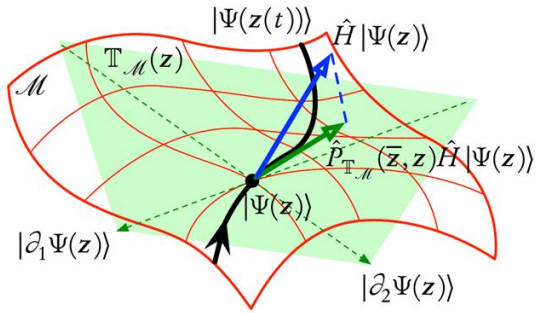


$$\tilde{\Phi} \approx \hat{H}\Psi(t)$$

- **adaptively optimize bond dimension**

Garcia-Ripoll, J. J. *New J. Phys.* 2006, 8, 305.

Time-dependent variational principle



$$\langle\delta\Psi|i\frac{\partial}{\partial t} - \hat{H}|\Psi\rangle = 0 \qquad \frac{\partial|\Psi\rangle}{\partial t} = -i\hat{P}\hat{H}|\Psi\rangle$$

$$\hat{P} = \sum_{i=1}^{N} \hat{P}[1:i-1] \otimes \hat{I}_i \otimes \hat{P}[i+1:N] - \sum_{i=1}^{N-1} \hat{P}[1:i] \otimes \hat{P}[i+1:N]$$

- **energy conservation**
- **wavefunction norm conservation**
- **no large tensor decomposition**

Haegeman, J.; Lubich, C.; Oseledets, I.; Vandereycken, B.; Verstraete, F. *Phys. Rev. B.* 2016, 94, 165116.

Temperature effect and density matrix evolution

Purify any density matrix to a wavefunction in an enlarged space $P \otimes Q, Q \equiv P$

$$\rho = \sum_l w_l |l\rangle_P \langle l|_P = \mathrm{Tr}_Q |\Psi\rangle\langle\Psi|, |\Psi\rangle = \sum_l \sqrt{w_l} |l\rangle_P |l\rangle_Q$$ **thermo field dynamics**

Thermal equilibrium density matrix at β

$$\rho_\beta = \frac{e^{-\beta H_P}}{Z_\beta} \qquad |\Psi(\beta/2)\rangle = \sum_k \frac{e^{-\beta/2 \hat{H}_P}}{\sqrt{Z_\beta}} |k\rangle_P |k\rangle_Q$$

normalized

$$\langle\Psi(\beta/2)|\Psi(\beta/2)\rangle = 1$$

$$\beta = 0 \qquad |\Psi(0)\rangle = \prod_i \sum_{\sigma_i} \frac{1}{\sqrt{d_i}} |\sigma_i\rangle_P |\sigma_i\rangle_Q$$ **maximally entangled state, M_o=1**

imaginary time SE:

$$-\frac{\partial}{\partial\tau}\Psi(\tau) = \hat{H}_P \Psi(\tau) \qquad \tau = 0 \rightarrow \beta/2$$ **normalization after each time-step**

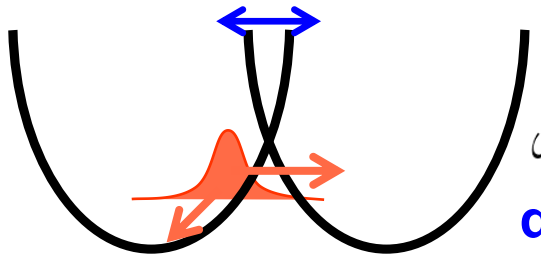
Takahasi, Y.; Umezawa, H. Collective Phenomena; Gordon and Breach, Science Publishers: London, 1975; Vol. 2, pp 55−80.
Feiguin, A. E.; White, S. R. *Phys. Rev. B* 2005, 72, 220401.
Verstraete, F.; Garcia-Ripoll, J. J.; Cirac, J. I. *Phys. Rev. Lett.* 2004, 93, 207204.
Zwolak, M.; Vidal, G. *Phys. Rev. Lett.* 2004, 93, 207205.

Spin-boson model with sub-Ohmic spectral density

SBM

electronic coupling Δ

delocalization



relaxation

localization

$$H = \epsilon\sigma_z + \Delta\sigma_x + \frac{1}{2}\sum_i (p_i^2 + \omega_i^2 q_i^2) + \sigma_z \sum_i c_i q_i$$

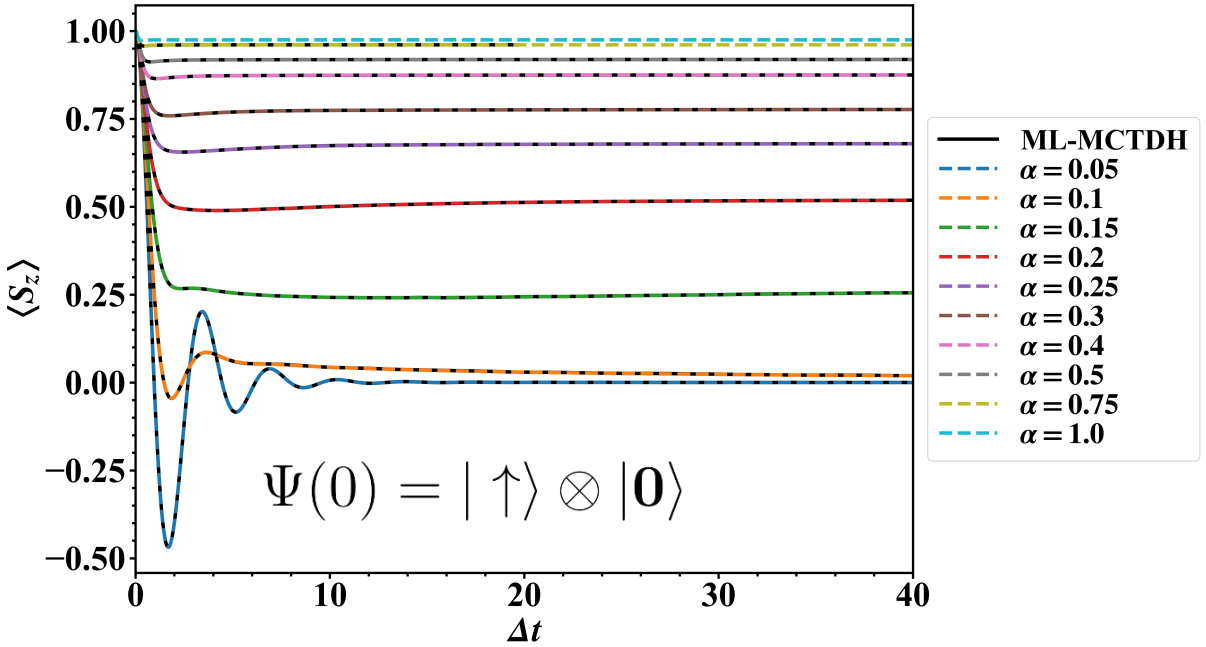
sub-Ohmic spectral density $\mathcal{J}(\omega) = \frac{\pi}{2}\alpha\omega^s\omega_c^{1-s}e^{-\omega/\omega_c}$

$$\omega_c = 20, s = 0.5, \epsilon = 0, \Delta = 1, T = 0$$

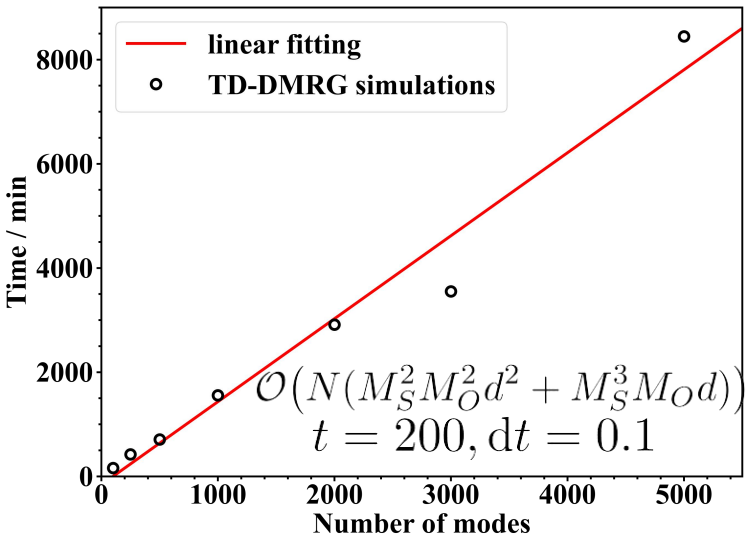
delocalization to localization

phase transition

basis d	10
bond dimension M	20
modes N	1000



Computational cost with respect to the number of modes

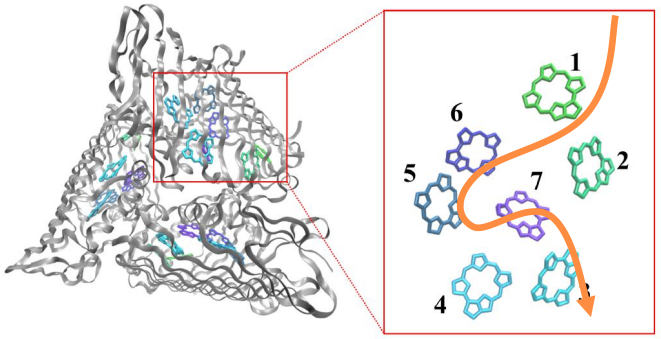


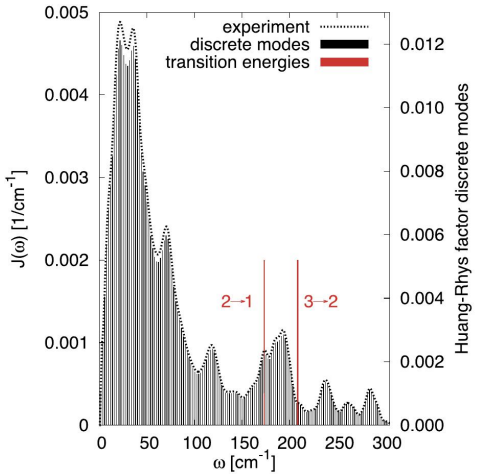
Not published

ML-MCTDH: Wang H. B. and Thoss M., Chem. Phys. 2010, 370, 78

Energy transfer in 7-site Fenna–Matthews–Olson complex

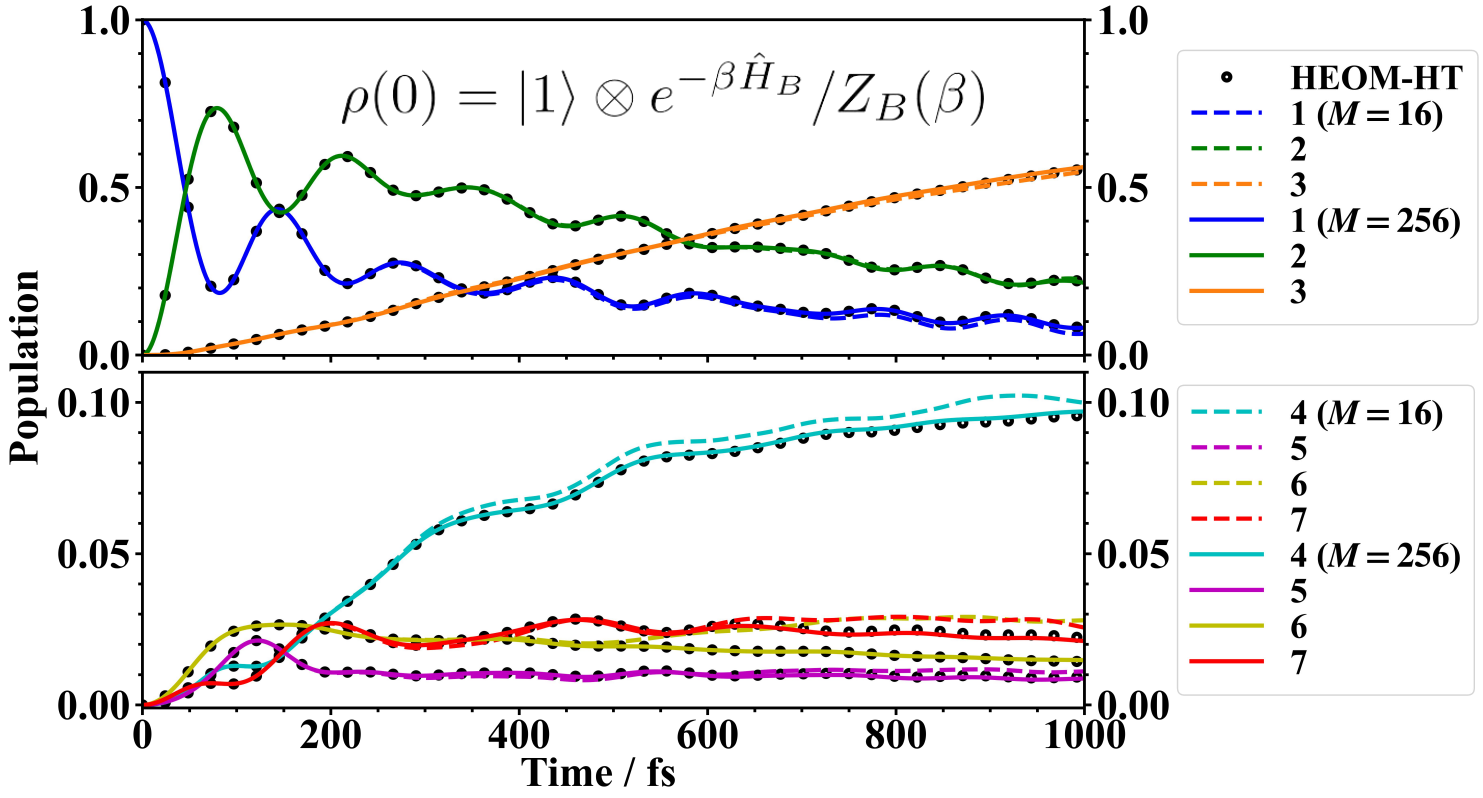
$$H = \sum_m \varepsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n + \frac{1}{2} \sum_{mi} (p_{mi}^2 + \omega_{mi}^2 q_{mi}^2) + \sum_{mi} c_{mi} q_{mi} a_m^\dagger a_m$$





$d = 10, N = 74 \times 7, T = 77\,\mathrm{K}$

$\rho(0) = |1\rangle \otimes e^{-\beta \hat{H}_B} / Z_B(\beta)$



HEOM-HT: Yan, Y.; Xu, M.; Li, T.; Shi, Q. *J. Chem. Phys.* 2021, 154, 194104.
Li, W.; Ren, J.*; Shuai, Z. *J. Chem. Phys.* 2020, 152, 024127. (JCP Editors' Choice 2019)

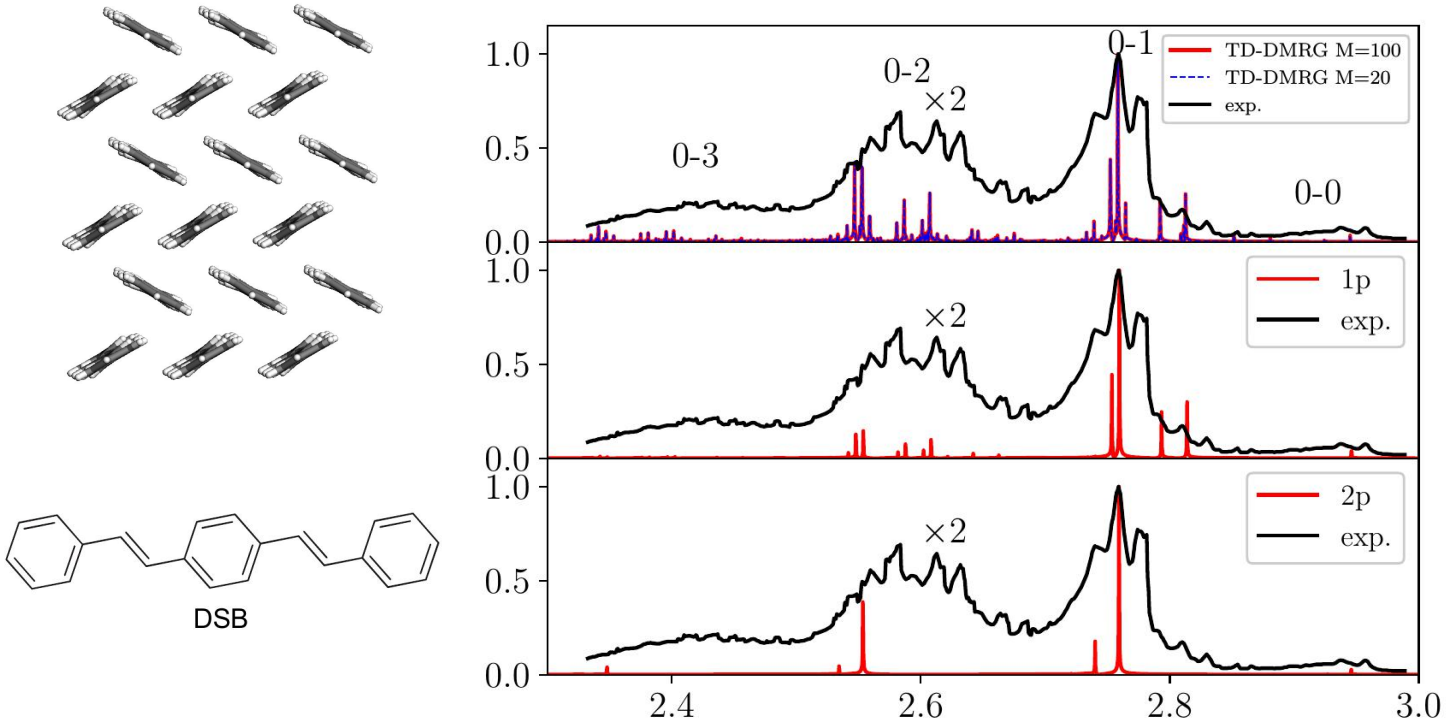
Emission of DSB crystal

	N molecules	N modes	N phonons	dimension of Hilbert space
TD-DMRG	18	14	10	18×10^{252}
1-particle	18	5	4	18432
2-particle	18	2	4	73728

$$\sigma(\omega) \propto -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\infty} C(t)e^{i\omega t}dt$$

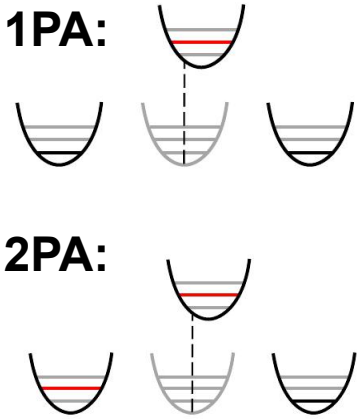
$$C(t) = -i\theta(t)\langle[\hat{\mu}(t), \hat{\mu}]\rangle_{\mathrm{gs,ex}}$$

correlated initial state $\hat{H}|\psi\rangle = E|\psi\rangle$



1PA:

2PA:

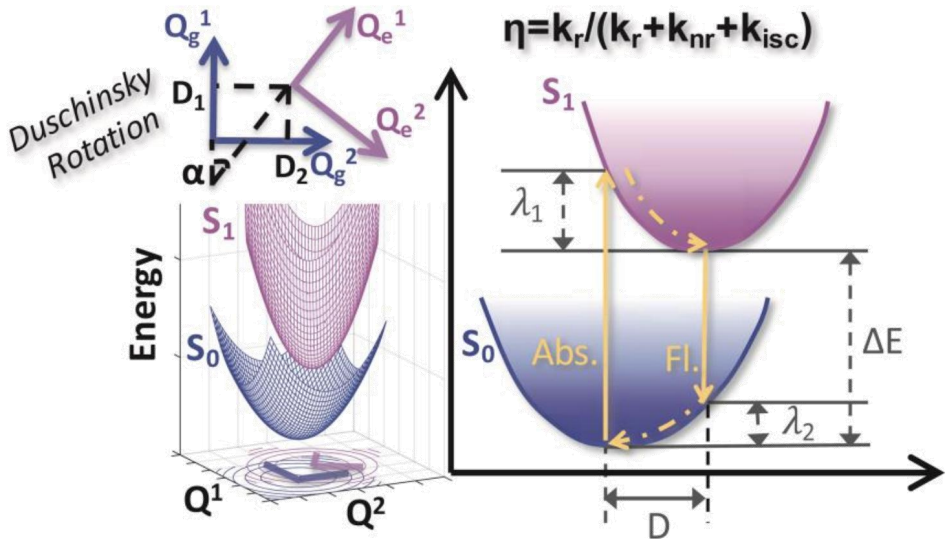


truncated Hilbert space

Spano, F. C. *Acc. Chem. Res.* 2010, 43, 429.

Exp: 1.4 K Wu, C.; Delong, M.; Vardeny, Z.; Ferraris, J. *Synth. Met.* 2003, 137, 939.
Ren, J.; Shuai, Z.; Kin-Lic Chan, G. *J. Chem. Theory Comput.* 2018, 14, 5027.

Anharmonic effect in molecular photophysics



$$\hat{H}_{i/f} = \hat{T} + V_{i/f}(q)$$

$$q_{i,m} = \sum_l J_{ml} q_{f,l} + \Delta q_{i,m}$$

displacement, torsion, rotation

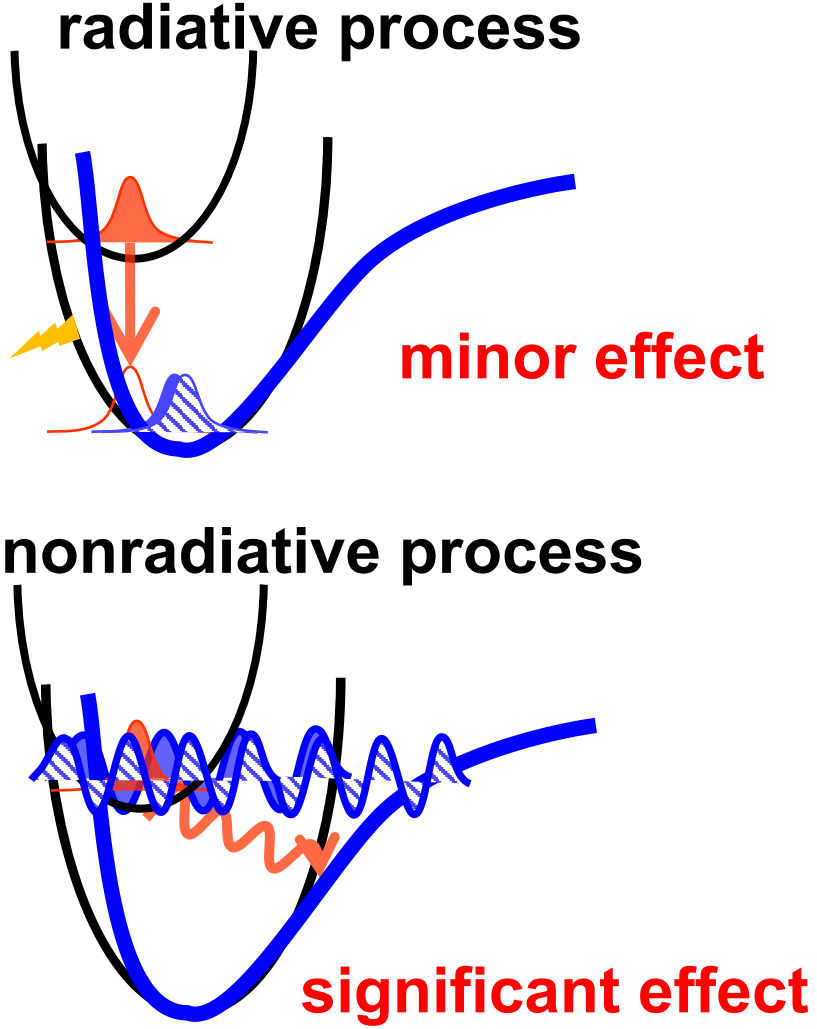
weak nonadiabatic coupling regime (FGR is valid):

$$\Psi_{i/f}(r,q) = \phi_{i/f}(r;q) X_{i/f}(q)$$

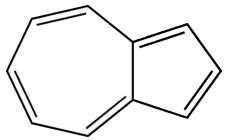
$$k_{ic} = \int_{-\infty}^{\infty} e^{i\Delta E_{ad} t} C(t)\, dt \qquad \hat{H}_1 = -\sum_l F_{fi}^l(q) |\phi_f\rangle\langle\phi_i| \frac{\partial}{\partial q_l} + \text{h.c.}$$

$$C(t) = \langle \hat{H}_1(t)\hat{H}_1 \rangle_T = \text{Tr}\left(\frac{e^{-\beta \hat{H}_i}}{Z(\beta)} e^{i\hat{H}_i t} \hat{H}_1 e^{-i\hat{H}_f t} \hat{H}_1\right) \qquad F_{fi}^l(q) = \langle \phi_f | \frac{\partial}{\partial q_l} | \phi_i \rangle_r$$

Peng, Q.; Yi, Y.; Shuai, Z.; Shao, J. *J. Chem. Phys.* 2007, 126, 114302.



N-mode representation (n-MR) theory



azulene (48D)

The first anti-Kasha emissive molecule

$S_1 \rightarrow S_0$ internal conversion is very fast

- **1-mode, 2-mode, 3-mode... hierarchical expansion**

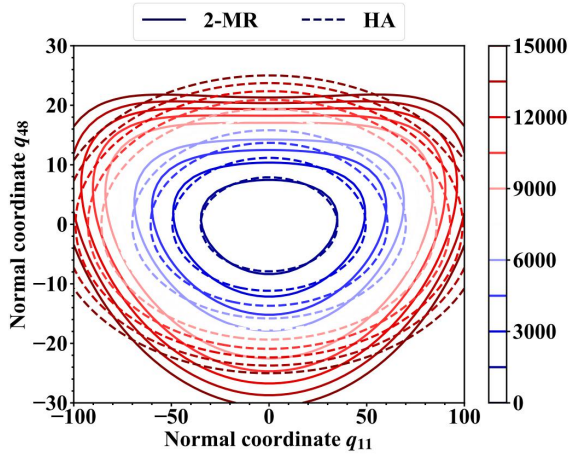
$$V(q_1, q_2, \cdots, q_N) = V^{(0)}(\boldsymbol{q}^{\mathrm{ref}}) + \sum_i V^{(1)}(q_i; \boldsymbol{q}^{\mathrm{ref}}_{l\neq i}) + \sum_{i<j} V^{(2)}(q_i, q_j; \boldsymbol{q}^{\mathrm{ref}}_{l\neq ij}) + \cdots$$

$$V^{(1)}(q_i; \boldsymbol{q}^{\mathrm{ref}}_{l\neq i}) = V(q_i; \boldsymbol{q}^{\mathrm{ref}}_{l\neq i}) - V^{(0)}(\boldsymbol{q}^{\mathrm{ref}})$$

$$V^{(2)}(q_i, q_j; \boldsymbol{q}^{\mathrm{ref}}_{l\neq ij}) = V(q_i, q_j; \boldsymbol{q}^{\mathrm{ref}}_{l\neq ij}) - V^{(1)}(q_i; \boldsymbol{q}^{\mathrm{ref}}_{l\neq i}) - V^{(1)}(q_j; \boldsymbol{q}^{\mathrm{ref}}_{l\neq j}) - V^{(0)}(\boldsymbol{q}^{\mathrm{ref}})$$

Li, G.; Rosenthal, C.; Rabitz, H. *J. Phys. Chem. A* 2001, 105, 7765.

- **reorganization energy (check the quality of the PES) units: cm^{-1}**



	4-points method	harmonic	1-MR	2-MR
S_0 surface	3481.9	3399.2	3421.4	3495.7
error		-82.7	-60.5	13.8

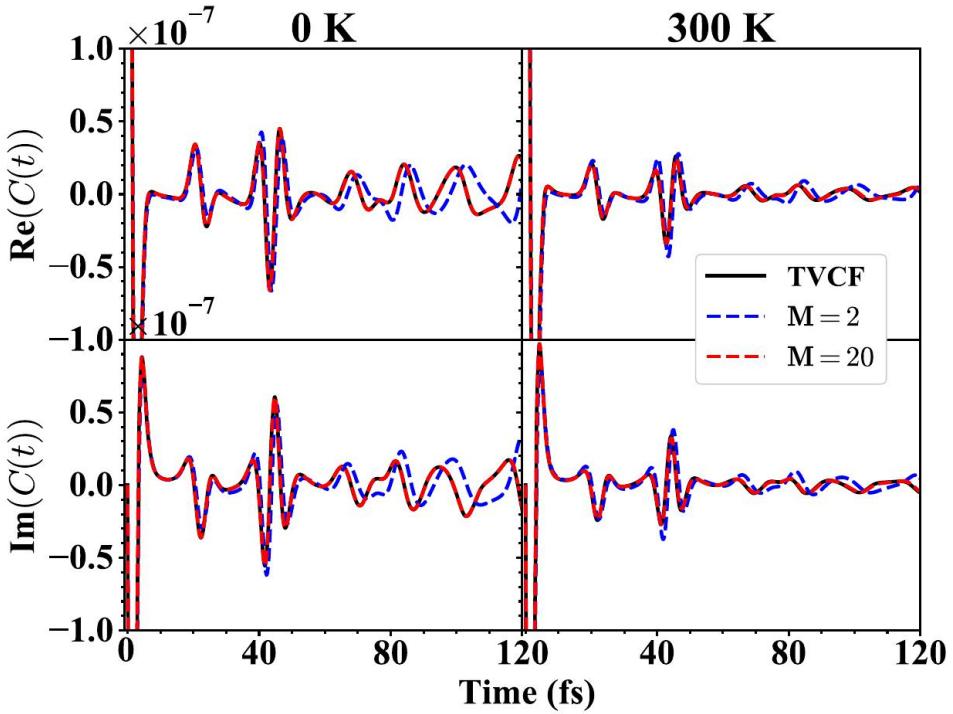
b3lyp/6-31g(d)

k_{ic} of azulene from S_1 to S_0

Method	k_{ic} ($\times 10^{10}$ s^{-1}) at 0 K			k_{ic} ($\times 10^{10}$ s^{-1}) at 300 K		
	HA	1-MR	2-MR	HA	1-MR	2-MR
TVCF	0.79	-	-	1.00	-	-
TD-DMRG	0.79	1.47 (186%)	3.56 (451%)	0.97	1.86 (192%)	4.53 (467%)

t = 425 fs, SHO basis = 20
100 cm^{-1} Gaussian broadening

- **1-MR is 2 times the rate of HA**
- **2-MR is 4 times the rate of HA**



HA: Thermal Vibration Correlation Function approach (TVCF) is analytically exact

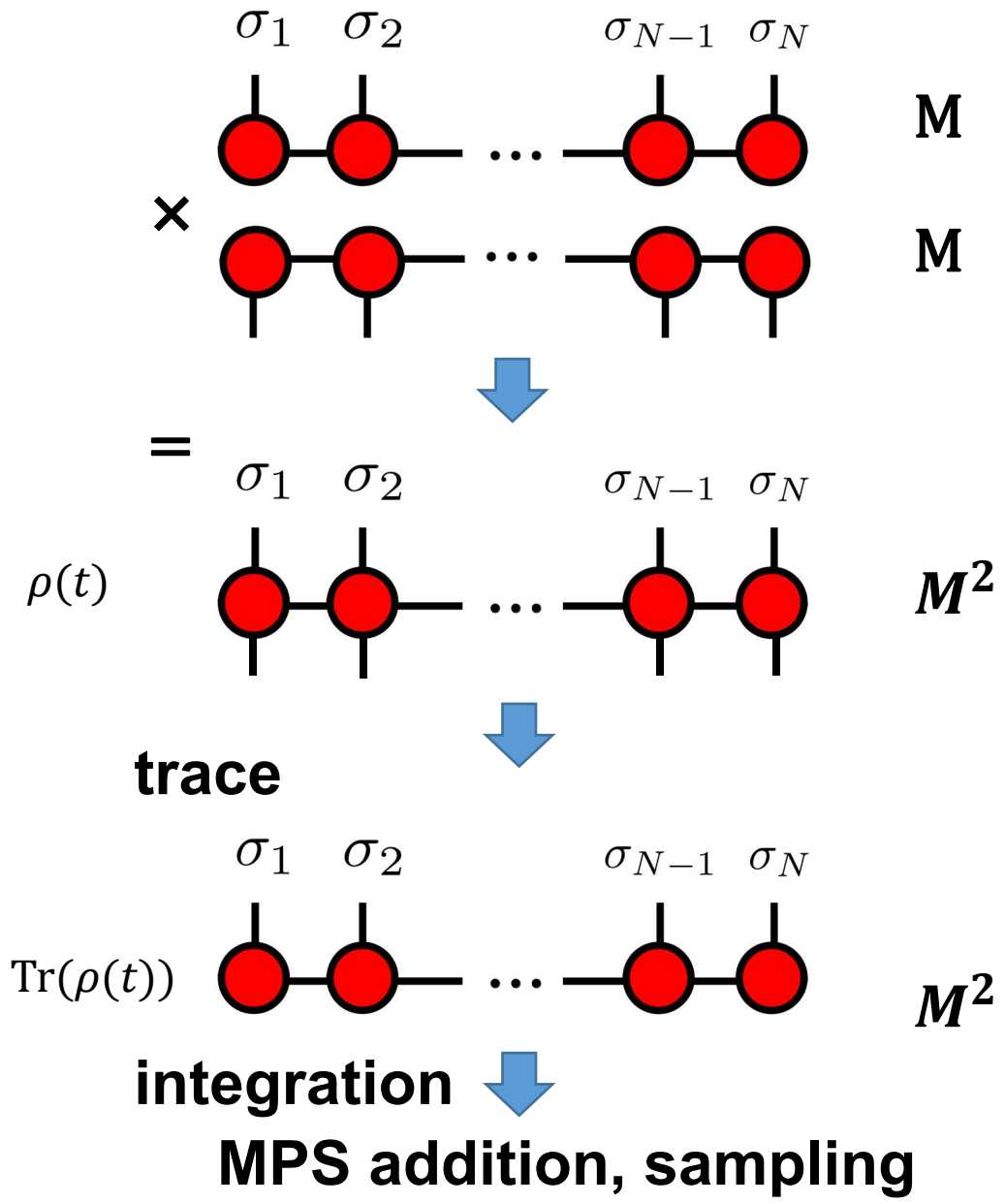
Wang, Y.; Ren, J.; Shuai, Z. *J. Chem. Phys.* 2021,154, 214109.

Final state resolved transition rate

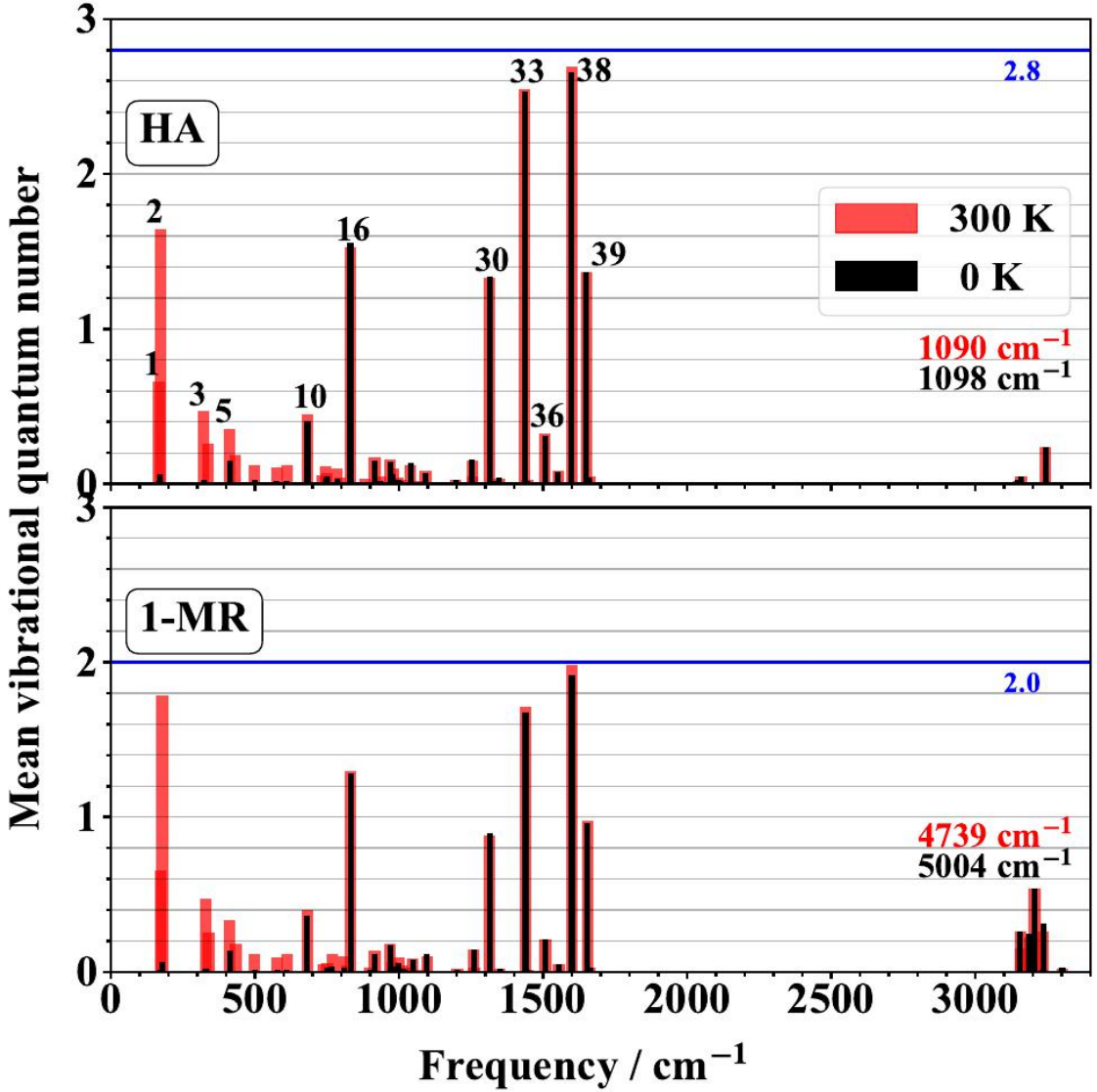
$$
\begin{aligned}
k &= \int_{-\infty}^{\infty} \langle \psi_0 | \hat{H}_1(t) \hat{H}_1 | \psi_0 \rangle dt \\
&= \int_{-\infty}^{\infty} \mathrm{Tr}(\hat{H}_1 | \psi_0 \rangle \langle \psi_0 | \hat{H}_1(t)) dt \\
&= \int_{-\infty}^{\infty} \sum_{\{\sigma\}} \langle \{\sigma\} | \rho(t) | \{\sigma\} \rangle dt \\
&= \sum_{\{\sigma\}} \int_{-\infty}^{\infty} \langle \{\sigma\} | \rho(t) | \{\sigma\} \rangle dt \\
&= \sum_{\{\sigma\}} k(\psi_0 \to \{\sigma\})
\end{aligned}
$$

If the primitive basis $\{\sigma\}$ is the eigenbasis, the final state resolved rate corresponds to each configuration coefficient of the integral of $\rho(t)$.

- HA: SHO (exact)
- 1-MR: VSCF modal (exact)



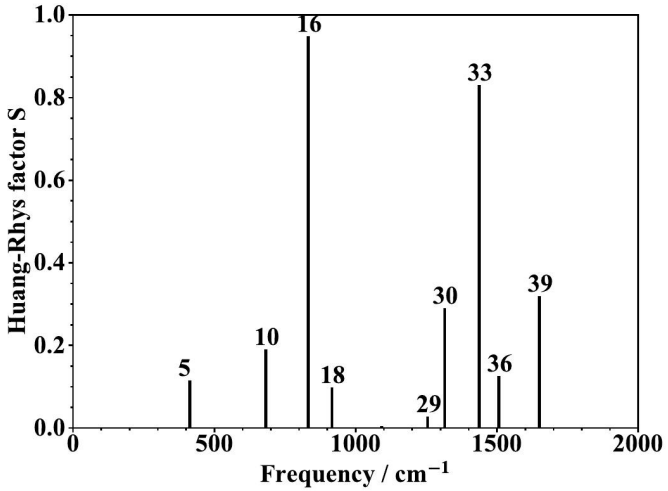
Mean vibrational quantum number



$$p_{v_l} = \sum_{\text{all}\, v_{k,k\neq l}} \frac{k_{v_1 v_2, \cdots, v_l, \cdots v_N}}{k_{\text{ic}}}$$

$$\bar{v}_l = \sum_{v_l} p_{v_l} v_l$$

$$\bar{\varepsilon}_l = \sum_{v_l} p_{v_l} \varepsilon_{v_l}$$



- **High frequency C-H vibrations with ~0 Huang-Rhys factor are able to accept energy;**
- **the mean vibrational quantum number of the other modes decreases;**

the FC factor is larger and the rate is faster.

Ren, J.; Wang, Y.; Li, W.; Jiang, T.; Shuai, Z.* *Chinese J. Chem. Phys.* **2021**, accepted.

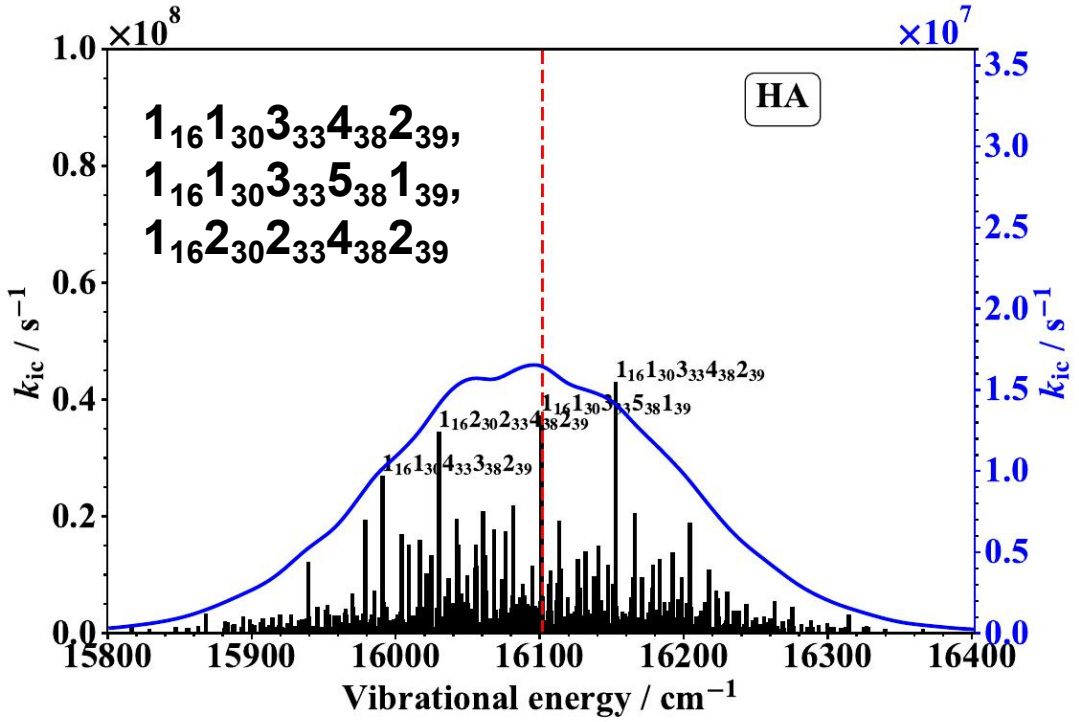
Contribution of each final state

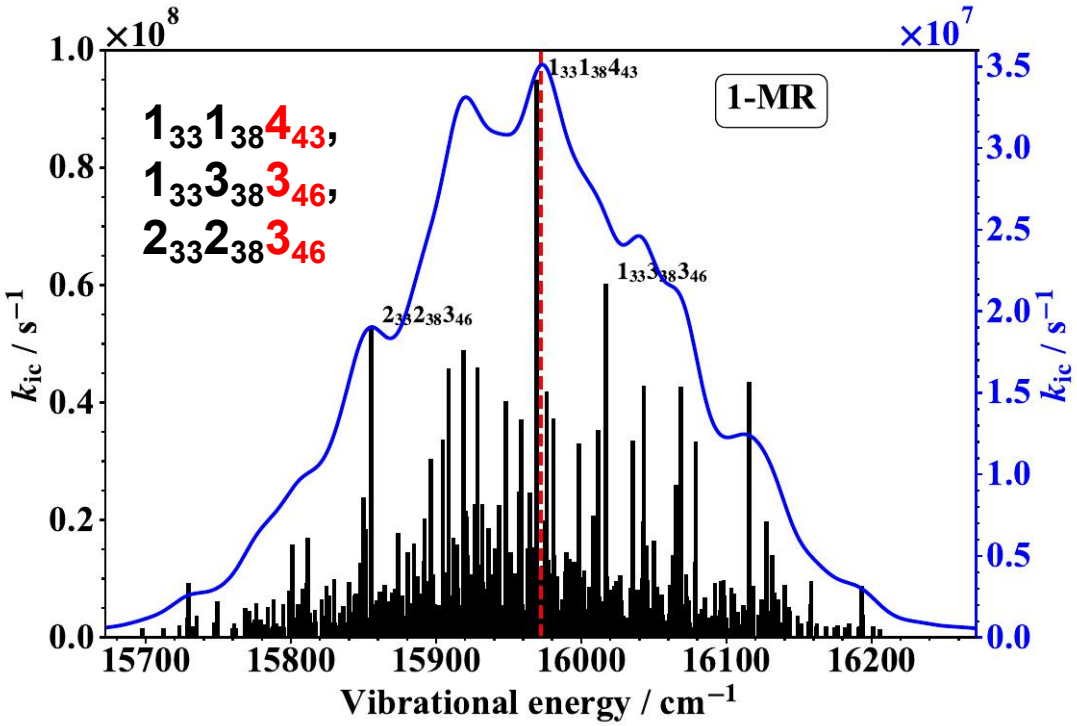
Monte Carlo sampling to get 5×10^5 configurations (in total 10^{48})

PES	HA	1-MR
Percentage of total rate	71.5%	70.8%

$$\rho(\omega) = \sum_i k_i \delta(\omega - \omega_i)$$

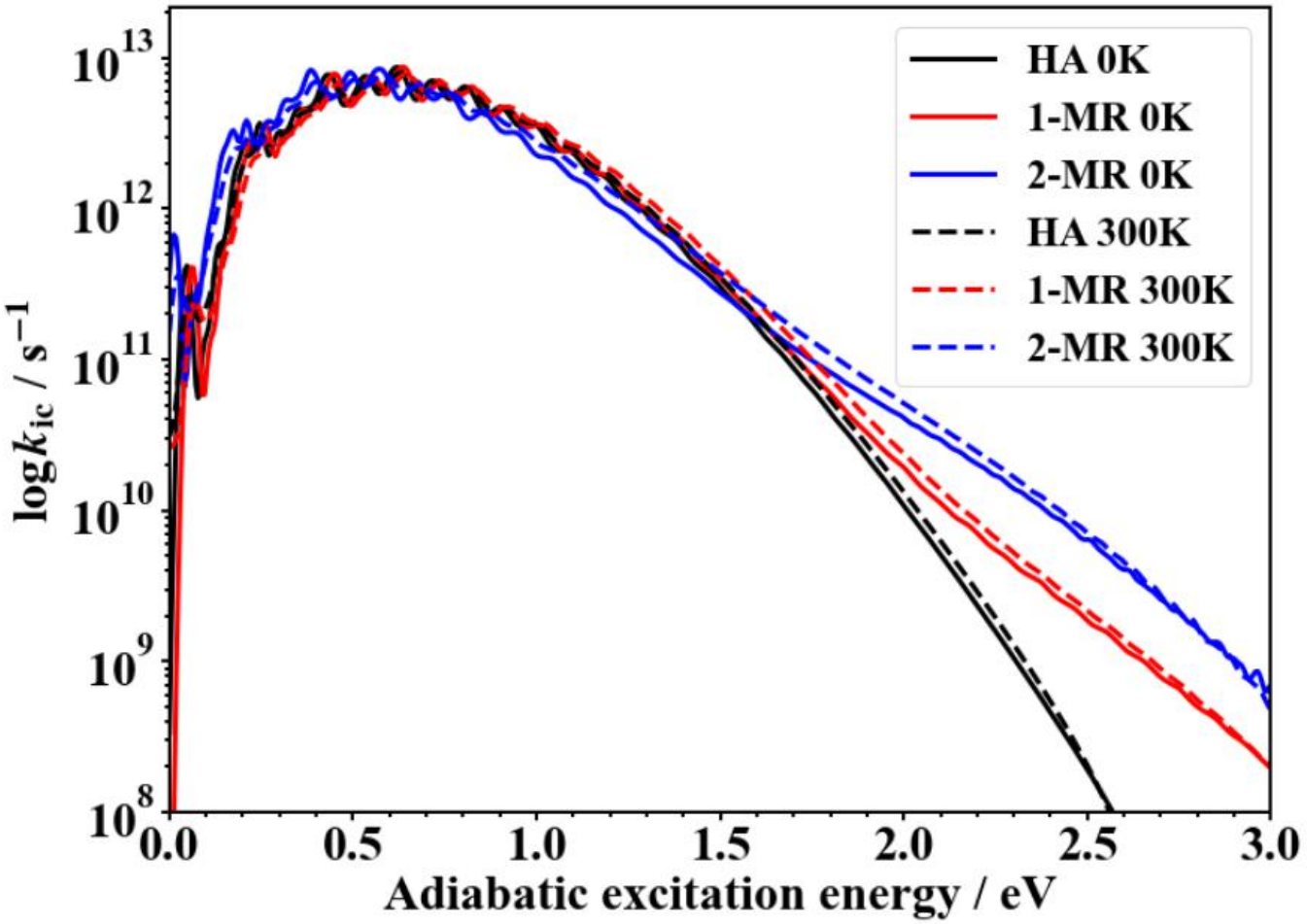
10 cm^{-1} Gaussian broadening





Ren, J.; Wang, Y.; Li, W.; Jiang, T.; Shuai, Z.* *Chinese J. Chem. Phys.* **2021**, accepted.

k_{ic} of different energy gap



M=60
d=20 SHO

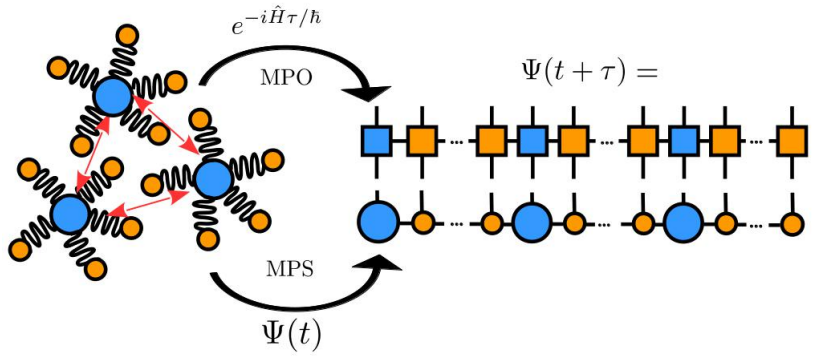
The larger the energy gap, the more pronounced the anharmonic effect.

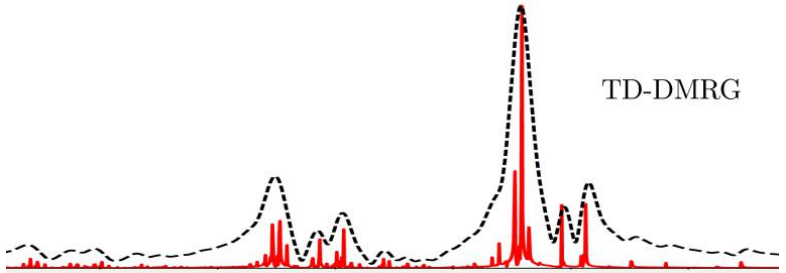
Ren, J.; Wang, Y.; Li, W.; Jiang, T.; Shuai, Z.* *Chinese J. Chem. Phys.* 2021, accepted.

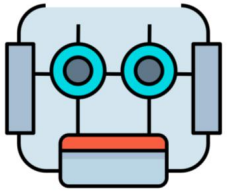
Summary

High-accurate, high-efficient TD-DMRG algorithm for high-dimensional quantum dynamics at both zero and finite temperature.

- **system-bath model with harmonic bath and linear coupling**
- **molecular photophysical properties on anharmonic PES**







RENORMALIZER

https://github.com/shuaigroup/Renormalizer

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Thanks for your attention!